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# Critique of Methods to Measure Dry Deposition Workshop Summary

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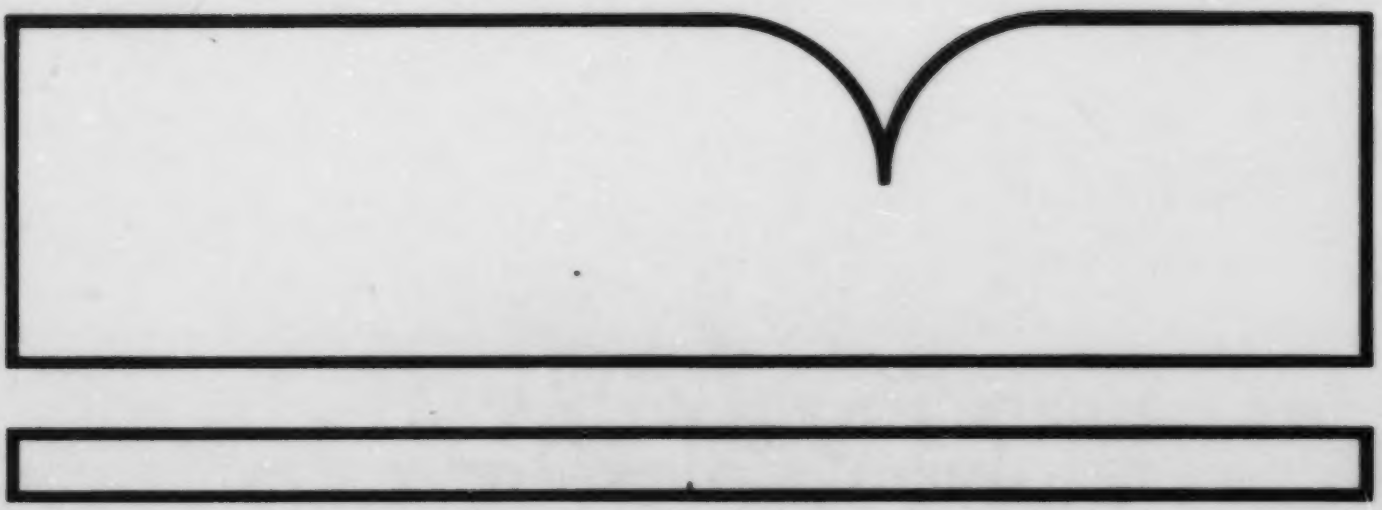

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October 1980

# CRITIQUE OF METHODS TO MEASURE DRY DEPOSITION
## Workshop Summary

by

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and

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16. ABSTRACT

At the Workshop on Dry Deposition Methodology, held December 4 and 5, 1979, at the Argonne National Laboratory in Argonne, Illinois, dry deposition measurement techniques were assessed for routine monitoring use. A majority opinion was reached that commonly-used techniques such as surrogate surfaces and collection vessels are not sufficiently accurate for use in networks, because the highly varied properties of the natural surfaces of interest cannot be simulated adequately. Further research was recommended on dry deposition parameters in order to estimate dry deposition rates, if possible, from measurements of atmospheric concentrations at a single height, together with observations of surface properties and micrometeorological parameters. The ability to perform such investigations in the field is critically dependent upon advances in chemical and physical capabilities to provide methods with standard relative errors of less than 1 percent for a single instrument on successive measurements, or with time responses of less than 1 second. These requirements are not being achieved for many pollutant species. At present, the most promising methods for monitoring are eddy accumulation, modified Bowen ration, and variance. Alternative views are presented in Appendix C.

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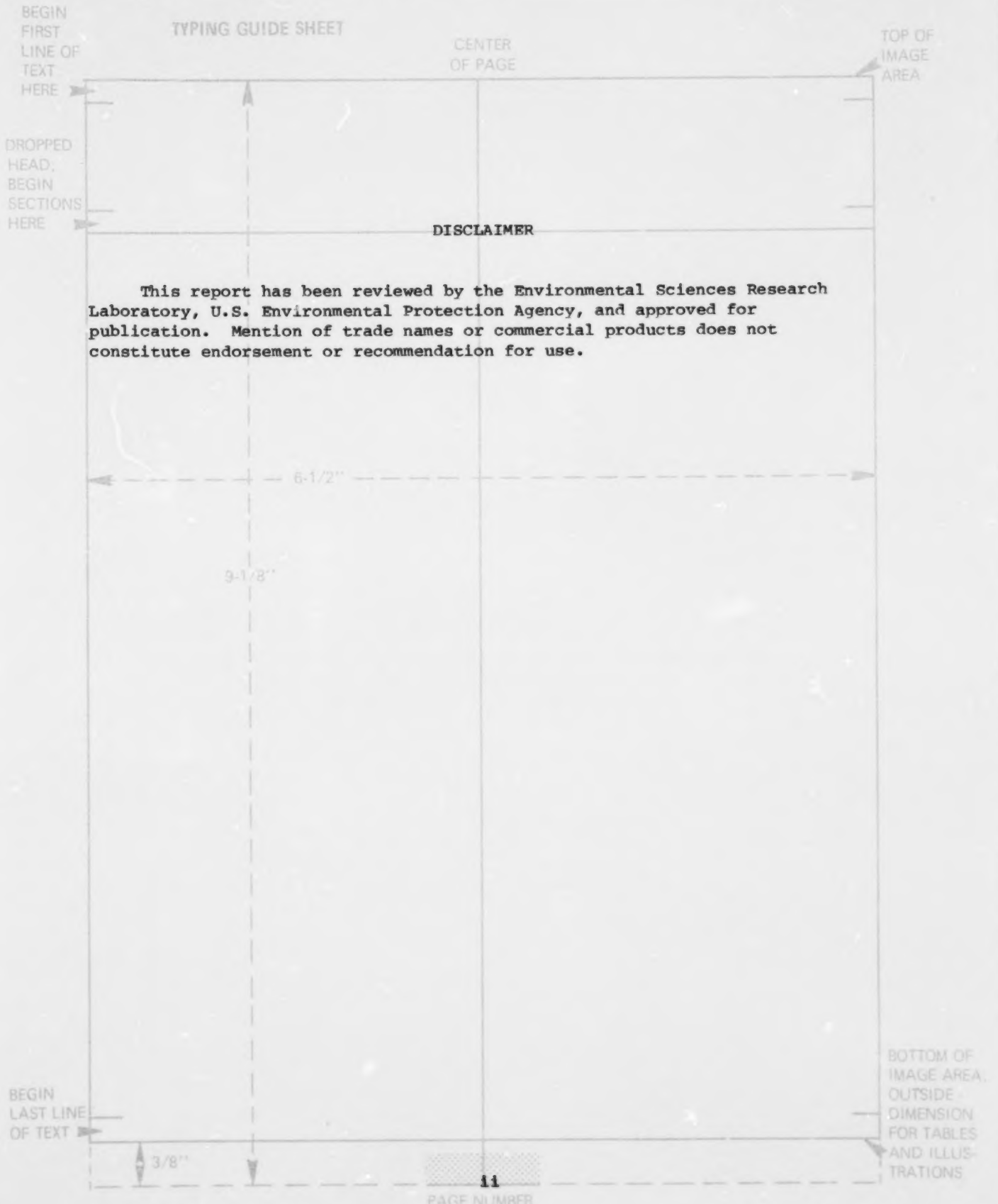


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## FOREWORD

Responsible and effective management of our nation's ecosytems requires a quantitative understanding of the relationships between emissions of air pollutants from all types of sources and air quality; transport, transformation, and removal processes are involved. The Environmental Sciences Research Laboratory investigates these source-air quality relationships for the purpose of providing the technical basis for air pollution control strategies by

- conducting laboratory and field investigations of the chemistry, physics, and meteorology of air pollutants
- developing techniques and instrumentation for the measurement and characterization of air pollutants in ambient air and in source emissions.

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During the past several years, the public has become aware of the acid rain problem and the subsequent acidification of aquatic systems. Scientists suspect that acidification results from the long-range transport/transformation and deposition of acidic gases and aerosols. Wet and dry deposition pathways of acids are presently thought to be comparable, but serious reservations exist in accepting dry deposition estimates inferred from air quality measurements on the basis of measurements by dry deposition monitors presently in use. For these reasons, the U.S. Environmental Protection Agency sponsored a workshop for technical experts on dry deposition phenomena to critique current techniques and to recommend research and development.

Dr. Alfred H. Ellison
Director
Environmental Sciences Research Laboratory

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## PREFACE

Within the last decade, there have been improvements in urban air quality, but deterioration has occurred on the regional scale. Contributing factors are the shifting of electrical power generation to rural areas and the use of tall stacks. There has been a recent awareness of the decline of visual quality in the eastern United States, and a serious concern for what now appears to be a significant trend of increasing quantities of strong acids removed from the atmosphere by both wet and dry deposition.

Continued industrial growth is of great importance to us as Americans wishing to preserve and expand our personal economic well-being. However, protection of atmospheric quality is also an important consideration, and has been expressed through the Clean Air Act and its amendments. The conflict between these two important concerns can rationally be resolved through an environmental air quality management program. However, to be effective and acceptable politically, air pollution control strategies need to be devised that are based upon defensible procedures. Two important methods providing a basis for air pollution control programs are predictive modeling and environmental monitoring; these two activities provide the mechanism for selective control of those emissions that give rise to unacceptable loss of air quality and undesirable ecological effects.

Knowledge of dry deposition rates is necessary for the successful application of predictive models. Of equal importance is the routine or semi-routine monitoring of dry deposition of pollutants, especially the strong mineral acids. Presently, our knowledge of rates is too limited, and our ability to monitor in networks is severely restricted.

There has been a continuing interest in dry deposition for many years. Theory, methodology, and experimental results have been reviewed in an Energy Research and Development Agency symposium (1974) and in many subsequent papers. However, it was not the intent of this workshop to attempt to provide an updated summary of the status of this research field. Instead, the U.S. Environmental Protection Agency (EPA) wished to focus its attention on two principal items:

1. *The identification of methods that might lead to the development of a routine technique for measuring dry deposition at monitoring stations, and*

2. *Fresh or improved approaches to research grade measurement of dry deposition rates.*

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Because of the shortness of time and limited resources, goals can be met only by adopting a narrow sense of purpose and by rejecting extraneous, yet important, topics. It is important to understand what the purpose of this workshop was as well as what it was not.

The purpose was:

*1. To identify the advantages and disadvantages of current methods for measurement of dry deposition of air pollutants.*

*2. To speculate on the potential of other methods.*

*3. To make recommendations to EPA for research and development in regard to (a) research methods, instruments, field measurements, and tests, and (b) methods for evaluating and monitoring dry deposition on a routine or semi-routine basis.*

The purpose was not:

*1. To certify the methods and results obtained by the participants or others, or to lobby for a favorite method.*

*2. To address ecological effects.*

*3. To address transport modeling.*

*4. To obtain a consensus on everything.*

Regrettably, in the interest of obtaining a manageable level of verbal exchange and a timely pace, it was not possible to invite all who are active in this field or others with an interest in attending. Our intent was to select only one scientist to serve as a "representative" expert on a special method. There is a critical limit above which efficiency declines. I take the responsibility for defining it and attempting to keep the group small.

Some of the participants may have wondered why they were invited. The reason is of interest, as it is in itself a reflection of the state-of-the-art. As more and more becomes known about the proccesses involved in air-surface interaction, it is becoming increasingly clear that the critical consideration might not be physical but chemical or biological. For this reason, we have recognized the need to look carefully at what is known in the closely related fields of agrometeorology, forest methorology, etc. We could not hope to represent all of those related fields at this workshop. However, we certainly can take some first steps toward improving relationships.

There are other fields of endeavor that were certainly poorly represented here. We apologize and suggest that all we could do was represent these areas as best we could and boldly state our limitations.

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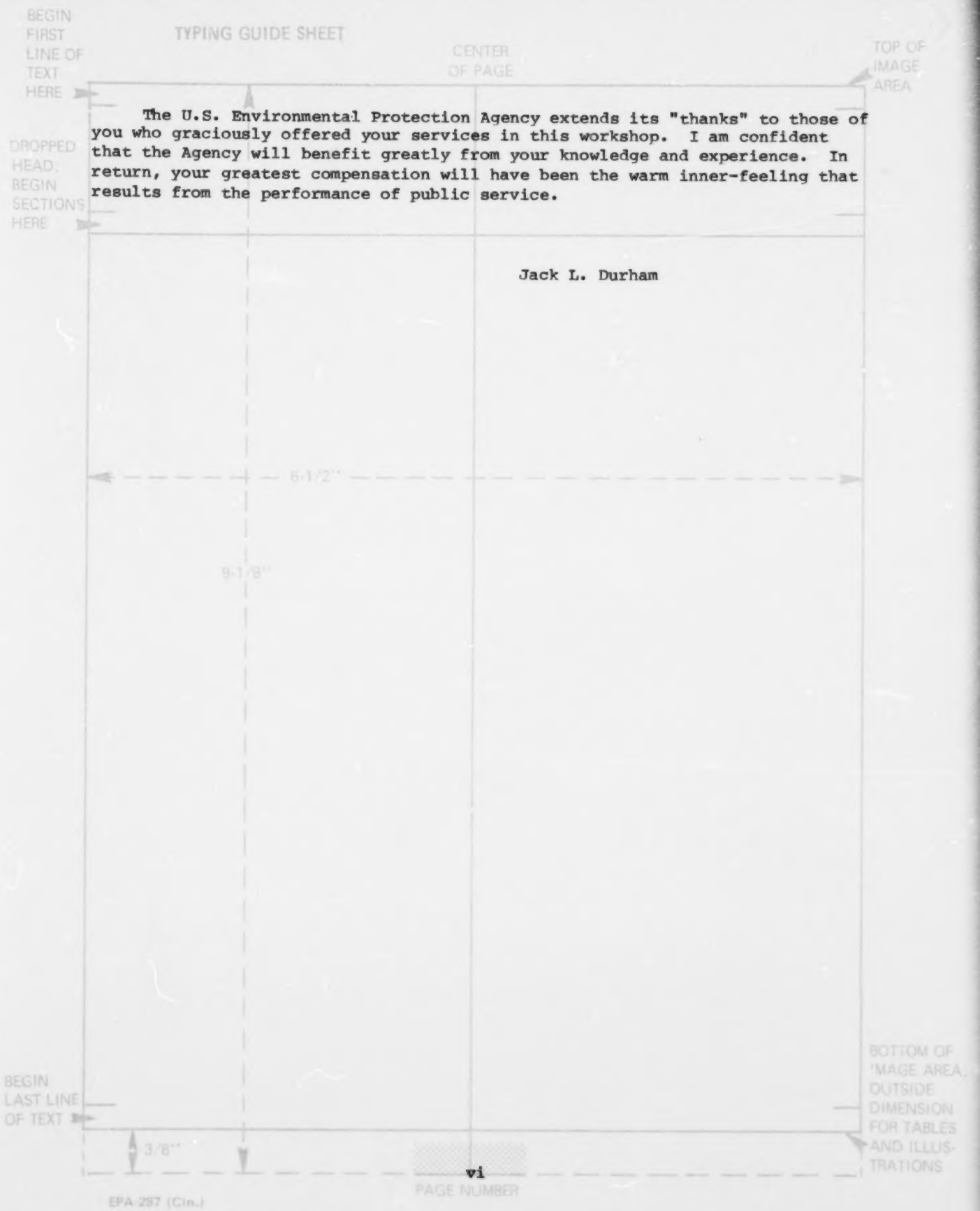


The U.S. Environmental Protection Agency extends its "thanks" to those of you who graciously offered your services in this workshop. I am confident that the Agency will benefit greatly from your knowledge and experience. In return, your greatest compensation will have been the warm inner-feeling that results from the performance of public service.

Jack L. Durham

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## ABSTRACT

At the Workshop on Dry Deposition Methodology, held December 4 and 5, 1979, at the Argonne National Laboratory in Argonne, Illinois, dry deposition measurement techniques were assessed for routine monitoring use. A majority opinion was reached that commonly-used techniques such as surrogate surfaces and collection vessels are not sufficiently accurate for use in networks, because the highly varied properties of the natural surfaces of interest cannot be simulated adequately. Further research was recommended on dry deposition parameters in order to estimate dry deposition rates, if possible, from measurements of atmospheric concentrations at a single height, together with observations of surface properties and micrometeorological parameters. The ability to perform such investigations in the field is critically dependent upon advances in chemical and physical capabilities to provide methods with standard relative errors of less than 1 percent for a single instrument on successive measurements, or with time responses of less than 1 second. These requirements are not being achieved for many pollutant species. At present, the most promising methods for monitoring are eddy accumulation, modified Bowen ratio, and variance. Regardless of the method employed, monitoring sites should be chosen that are representative of the surrounding areas in terms of surface properties, meteorological conditions, and pollutant characteristics. Alternative views are presented in Appendix C; in particular, research on certain applications of surrogate surface sampling is recommended, and concern indicated that unrealistic requirements of chemical analysis precision or response time have been allotted for the three "most promising methods for monitoring."


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We sincerely thank all the participants for their contributions without which this dry deposition methodology overview would not have materialized. Our appreciation is extended to Argonne National Laboratory, Argonne, Illinois, for providing the conference facilities and on-site conference support; Rebecca Spencer deserves special mention for overseeing the necessary preparations at Argonne. Our sincere appreciation is also extended to Olga Wierbicki of Northrop Services, Inc., Research Triangle Park, North Carolina, for coordinating the conference and editing the proceedings.

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## SECTION 1

## KEYNOTE ADDRESS

It is a particular pleasure to welcome participants in the U.S. Environmental Protection Agency (EPA) Workshop on Dry Deposition Methodology to Argonne National Laboratory (ANL). Not too many years ago, convening an EPA workshop at a Department of Energy (DOE) laboratory might have seemed somewhat unusual. Today, however, the environmental research responsibilities of these two agencies are increasingly recognized to be complementary: EPA is developing environmental criteria with a view toward minimizing unnecessary impact upon energy production, and DOE continues to maintain a policy for developing new energy technology in an environmentally acceptable manner.

More to the point of holding an EPA meeting at this DOE laboratory, the EPA Office of Research and Development now supports almost half of the work conducted by Argonne's Atmospheric Physics Section, and more than three quarters of the work of our Ecological Sciences Section. At the same time, DOE continues to fund related research and assessment programs dealing with the anticipated environmental impact of emerging energy technology in a number of ANL Divisions. Clearly, in ANL these two federal agencies have already found common ground.

Turning to the concerns of today's workshop, it is appropriate to remind ourselves at the outset that these deliberations on the measurement of pollutant deposition can benefit from our knowledge of the turbulent structure of the lower atmosphere. A number of now-classical, micrometeorological field experiments conducted during the last two decades have developed an extensive, basic understanding of the turbulent exchanges of heat, moisture, and momentum, which combine to maintain the kinetic and thermal energy budgets of the atmospheric boundary layer. In the present context of contributing to our understanding of the mechanisms of dry deposition, it is useful to remember that these same atmospheric turbulent exchange circulations also maintain local budgets of pollutant concentration: contaminants steadily depleted in the immediate vicinity of receiving surfaces by the deposition process are continuously resupplied by turbulent mixing from above. Each pollutant's special chemical and physical properties determine its particular affinity for the collecting surface and thus always control, and frequently dominate, the rate at which dry deposition removes that material from the air. However, in the equilibrium flux layer in the free air above the collecting surface, the aerodynamic pollutant-resupply rate equals the physically, chemically, or biologically dominated surface removal rate. This fact makes it possible to utilize the techniques of modern micrometeorological flux measurement to

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evaluate the rate of dry deposition, even though that removal is being accomplished by virtually unmeasurable, complex events that take place essentially in contact with the surface itself.

Preliminary results of pollutant eddy flux measurements are now being obtained at a number of laboratories, including ANL. Unfortunately, since the experimental equipment used is relatively complex, these micrometeorological methods are not suited to routine operation; therefore, the question before this workshop as to how dry deposition might best be monitored by a national network remains unsolved. Of course, a number of different dry deposition, pollutant collectors are now available, but their inherent limitations become clear when one considers the degree to which each of these devices either interferes with the aerodynamics of the pollutant resupply circulation, or fails to simulate the collection properties of nearby natural surfaces. The problem of selecting an operationally-feasible monitoring methodology is therefore particularly difficult, and one readily understands why dry deposition monitoring experiments to date have settled for a variety of solutions, no one of which is entirely satisfactory.

Nevertheless, since we do have an appreciable understanding of the aerodynamic phase of the dry deposition process, some technical guidance for monitoring methodology does exist. It remains to select a procedure that does not excessively violate either the aerodynamic or the collecting surface criteria (or, at least, one that only violates them in some reproducible way), and then to calibrate that method's relative collection efficiency over a range of physical and chemical pollutant characteristics, terrain and vegetation types, and meteorological conditions.

The monitoring problem is indeed difficult, but perhaps not entirely intractable. As Peter Medawar said of the useful tendency for new scientific principles to clear away masses of inconclusive experimental observations, "Since Newton formulated the law of gravity, we need no longer measure the fall of every apple." With more work, and some luck, conceivably something approaching this ideal might be accomplished for dry deposition.

Paul Frenzen
Associate Director
Radiological and Environmental
Research Division,
Argonne National Laboratory

## SECTION 2

## INTRODUCTION

The subject of dry deposition addresses all processes by which airborne contaminants are removed from the atmosphere at the surface of the earth, excluding those processes directly aided by precipitation. Ultimately, knowledge of the fate of pollutants is desired, particularly if the effects are harmful. For surface vegetation, for example, dry deposition can sometimes be equated to a dose that causes specific harmful effects, but often the effects of pollutants on biological systems occur after transport away from the initial surface contacted and after some change in chemical form. Since the surface flux of atmospheric contaminants affects concentrations downwind, dry deposition affects the extent of areas in which significant concentrations of pollutants are found. Thus, dry deposition exerts a strong, indirect influence on concentrations of pollutants found in precipitation and on interactions between pollutants.

Of concern here is primarily the rate of removal by dry deposition of pollutants in the atmosphere, to some extent their immediate fate, and less their effects, except those that aid in determining deposition rate. Methods used to assess or predict rates of dry deposition are extremely diverse, largely because the types of contaminants and surfaces vary greatly. Since the final assessment of dry deposition must take place for the actual environment considered, relevant studies have concentrated on experimental efforts in the field. Laboratory and purely theoretical work play a necessary role in understanding the processes that control dry deposition. Such understanding leads to a productive use of data from networks monitoring air quality, helps extrapolate present deposition results to pollutants not yet fully investigated, and leads to better parameterizations of surface removal for use in numerical models of pollutant distribution in the atmosphere.

The purpose of this report is to evaluate and summarize methods for determining routinely the dry deposition of gaseous and particulate pollutants over rather large areas. Section 5 presents the methods considered during the workshop and reflects the scientific knowledge and opinions of the participants. The needs of each method were kept in mind for measurements taken at scattered sites of uniform surface characteristics "typical" of the surrounding area. In the search for better methods of monitoring, a large amount of effort at the workshop was devoted to assessing methods normally used to parameterize the processes that control deposition. Section 6 describes an application of the parameterizations: using concentrations measured at air-quality monitoring stations to calculate the pollutant fluxes indirectly. Our current knowledge is, of course, inadequate to achieve this

goal for all important pollutants and surfaces; some of the research needs identified are briefly discussed in the second half of Section 6.

In conformity to the orientation of the workshop, the conclusions and recommendations in Section 4 are mainly concerned with the general scientific credibility of methods used to measure dry deposition. These recommendations, which are derived from the discussions in Sections 5 and 6, are highly critical of past and present attempts to monitor dry deposition routinely. No attempt is made to present a schedule of research that should be accomplished, since this subject was not explicitly addressed at the workshop. Indeed it would have been quite difficult, since competing research interests were purposefully represented. Specific details on research and monitoring methods (such as height of measurements) are not given if such details were not discussed explicitly. Finally, no recommendations are made as to which pollutants should be studied; this decision was not considered one of the tasks of the workshop, but one more appropriately to be made by those knowledgeable in health and ecological effects.

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## SECTION 3

## SUMMARY

This workshop report provides evaluations of various methods for estimating dry deposition of gaseous and particulate pollutants from the atmosphere to the surface of the earth. The intent is to provide the scientific information needed in order that sound decisions can be made on research, development, and coordination with regard to dry deposition. Existing and potential techniques for monitoring and parameterizing dry deposition are considered systematically and specific recommendations are given for each method on its present and potential usefulness. The viewpoints presented are based on and limited to opinions expressed during discussion that took place at the workshop. A priority of research needs was not established at the workshop and thus is not given here.

The current capabilities for monitoring dry deposition are felt to be inadequate because the methods now used, which usually employ surrogate surfaces or open vessels, do not give the deposition at the actual natural surface. Most of the workshop participants felt that "calibration" of such methods would not be successful or have very limited success. However, 20 to 30% of the scientists present who have been or are making original contributions to scientific research on dry deposition feel that the use of surrogate surfaces should be pursued in some fashion.

Fairly direct measurements of the net dry deposition can be obtained by measurement of the accumulation of certain chemicals in rather large areas over long periods of time. Because of the considerable amounts of effort necessary in application, this category of method clearly was never intended to apply to routine monitoring, although the results of such studies are quite useful in determining the fate of pollutants after reaching the surface.

Parameterization studies are directed toward understanding the relationships between vertical fluxes and the properties of pollutants, surfaces, and the atmosphere. Estimation of deposition rates needed for numerical simulations of pollutant behavior in the lower atmosphere usually are based on parameterizations of the deposition velocity (the ratio of flux to concentration at a specified height in the atmosphere). In this report, evaluations of numerous methods are presented. Of course, knowledge accumulated from parameterization studies might allow the use of pollutant concentrations monitored at a single height to estimate the vertical flux. To date, very few species of pollutants have been studied adequately to approach this goal. For example, the behavior of many species associated with strong acids has not been determined, because the chemical sensors presently available do not meet the specifications required by the techniques for

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measuring dry deposition. In many cases, there is no "sensor" but instead a procedure for chemical analysis best performed in a well-equipped laboratory. Usually, measurement procedures should be able to detect mean differences of 1 to 10% in successive samples to within an accuracy of 10%, in order to be useful to measure deposition rates. For flux measurement techniques that rely on detection of turbulent fluctuations in pollutant concentrations near the ground, the speed of response should be one second or less.

A simple, but accurate, method for monitoring dry deposition rates routinely is not available. Micrometeorological methods that have potential in this regard are the techniques of eddy accumulation, modified Bowen ratio, and variance methods. It should be remembered, though, that even if these or other methods prove very useful, the requirements on the selectivity and performance of chemical and physical sensors are still quite high and, in many cases, not yet achievable.

Sites selected for parameterization and monitoring studies ideally should be located in uniform terrain so that results are not affected by unusual features of the surface unique to that location. Monitoring sites, if they are to be effective, should be located at surfaces that are typical of the surrounding areas and that should have representative meteorological conditions and pollutant characteristics.

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## SECTION 4

## CONCLUSIONS AND RECOMMENDATIONS

The rate of dry deposition of atmospheric pollutants depends on many factors concerning the pollutants, surfaces, and atmospheric conditions. To evaluate methods that might potentially be used to monitor dry deposition, the roles of all contributing processes must be considered, at least in broad categories. The most important processes that affect deposition rates can often be identified as those corresponding to the largest resistance to vertical transport or uptake.

For small particles that are deposited by diffusion and impaction, deposition is strongly affected by the resistance of the quasi-laminar sublayer of air nearest to surface elements and by the microscale roughness and stickiness of the surface. For gaseous pollutants, the chemical and biological nature of a surface, as well as its physical configuration, often dominates the resistance to air-surface exchange. Processes of (re)emission and (re)suspension, which can greatly affect net deposition, are also highly dependent on surface properties. Hence, the following recommendation can be made:

> *1. Since use of artificial collecting surfaces does not simulate the net dry deposition of particles and gases to natural surfaces, it would be ill-advised to rely upon continued monitoring by "open pot" or various other types of surrogate surfaces. As a result, present capabilities to monitor dry deposition in a practical, yet accurate, manner are inadequate.*

Use of such surfaces has continued for estimating deposition of particles in some cases, simply because of the lack of better procedures that can be utilized with small cost and effort. Notably, knowledge on how to "calibrate" surrogate surfaces for gaseous or particulate deposition will probably never be obtained. At best, future efforts might relate the amount and type of material collected by a surrogate surface to a corresponding atmospheric concentration; it would then remain necessary to deduce surface fluxes from the inferred concentrations, not an easy task in most cases at present. It would probably be easier and more accurate over natural surfaces to measure concentrations directly rather than relying on artificial surfaces intended to simulate the actual surface.

In the process of choosing a site for monitoring (which assumes that a suitable monitoring technique is available), the importance of knowledge of surface characteristics must be emphasized. This consideration is reflected in another recommendation:

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*2. Sites chosen for monitoring should have a surface "typical" of the surrounding area; in the immediate vicinity of measurements, the surface should be a single uniform type. The condition of local vegetation and the general environmental conditions that affect the surface should be recorded.*

Obviously, there might be some difficulty in finding suitable sites in many locations. An additional requirement for site selection is:

*3. Monitoring sites should have pollutant and wind characteristics representative of the large surrounding area. Records should be maintained on the possible presence of pollutants from local sources and on local meteorological events such as precipitation, fog, and dewfall.*

The above two requirements for a good site imply that sites currently chosen for wet and dry deposition monitoring may not be adequate for obtaining representative estimates of dry deposition.

For monitoring, estimates of atmospheric resistance should be made routinely, since this resistance can control the transfer of pollutants that can be removed very efficiently by the surface, and since it is important to identify conditions of atmospheric decoupling at night, when turbulent vertical transport becomes exceedingly small. Provided a few essential measurements of atmospheric conditions are taken, micrometeorological formulations currently available are adequate for estimating the atmospheric resistance to vertical transport from a height of several meters to fairly close to the surface. We recommend the following:

*4. At each monitoring site, wind speed, atmospheric stability, and aerodynamic surface roughness should be determined, so that atmospheric resistances can be calculated and averaged over time intervals preferably not to exceed six hours; one-half to one hour is optimum.*

Current techniques intended to monitor dry deposition directly on a routine basis do not appear to be adequate. As stated above, surrogate collecting surfaces do not simulate surface conditions sufficiently well in most cases. An alternative method is to attempt to infer surface fluxes from pollutant concentrations measured at a single height; much work has already been devoted to develop the technical means to perform the needed measurements. Concentration measurements at one height, however, give no information on transfer processes in the atmosphere and at the air-surface interface. The following recommendation must therefore be made:

*5a. Concentration measurement at a single height should not be used by itself to provide a measure of dry deposition.*

The availability of measurements of some pollutant concentrations leads to questions as to what supporting information is required in order to interpret these measurements. Deposition rates can be estimated as the product of concentration and an appropriate deposition velocity. The latter

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quantity can be derived from accurate parameterizations of the deposition processes. As implied in Recommendation 4 above, micrometeorological aspects of parameterizations can be estimated fairly well above uniform sites. However, interactions of pollutants with the surfaces and the behavior of small particles in the interfacial air layers are not well understood. Therefore, to interpret past and future measurements of concentrations, at least until means sufficient for accurately and routinely monitoring dry deposition are developed, further research is needed. The following statement concludes Recommendation 5:

> *5b. In order to understand the relationships between vertical fluxes and concentrations measured at a single point, research on the parameterization of deposition processes should continue by use of a variety of theoretical approaches and experimental techniques in the laboratory and the field.*

Cooperative efforts between micrometeorologists, biologists, and aerosol scientists, among others, are required; many recent studies have not utilized such cooperation. For example, atmospheric investigations often do not study a minimum set of variables concerning pollutant and surface characteristics in order to elucidate the deposition processes. On the other hand, ecological studies often do not adequately document atmospheric conditions.

Based on present knowledge, it is possible to identify certain information that would need to be obtained routinely at monitoring sites in order to estimate deposition velocities for evaluating surface fluxes from concentrations measured at a single height. Of course, this needed information must also be obtained during the parameterization studies that form the basis for this possible monitoring technique. As already stated, wind speed at some specified height above the surface should be measured and atmospheric stability estimated, both for periods not to exceed six hours. The type, height, and condition of vegetation present should be known. Furthermore, consideration should be given to a number of other factors that appear to be important in the case of certain pollutant species. Soil moisture content can affect the uptake of some gaseous pollutants, especially over bare soil. Some measure of aridity and atmospheric stability might suffice to describe the gross aspects of physical environment that affect plant physiological functions; relative humidity and solar radiation measurements might suit this purpose. Other variables, particularly those dealing with conditions of vegetation, will probably be identified as important yet suitable for routine evaluation, as a result of future parameterization studies.

Deposition velocities depend on the type of pollutant as well as on surface and atmospheric conditions. For particles, studies have indicated that deposition is affected by diffusion, impaction, and sedimentation processes that are continuous functions of particle size in overlapping ranges. Measurements employing a single size fractionation of particles (and hence providing samples of "large" and "small" particles) are not satisfactory, since it is likely that the course and fine fractions each must be resolved into several size classes. Gases can be considered in categories of similar chemical properties only to a limited extent. Thus, to infer dry

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deposition from measurements of concentration at a single height, direct measurement of each pollutant of interest is required. The possible importance of (re)suspension and (re)emission processes further underlies this need.

To perform parameterization research such as implied in Recommendation 5b, one would surmise that there are or will be available methods to measure reliably the deposition rates. In that case, the measurement techniques might themselves offer the best means to monitor deposition rates. The corresponding recommendation reads as follows:

*6. Techniques used in field parameterization studies should be developed and examined for applicability to routine monitoring.*

The methods most recommended are micrometeorological in nature. Verification of the techniques requires some direct measurements of accumulation at the surface; box-budget experiments, though usually too inaccurate, may someday provide an estimate of errors. The following statement, at least, can be made:

*7. Although micrometeorological methods offer the promise of providing a direct and precise measure of dry deposition, experimental complexity and sensor inadequacies combine to reduce confidence in them. At this time, no micrometeorological method can be accepted with absolute confidence. There is need for continued intercomparison and comparison with other methods.*

Fluxes of particles large enough to be affected significantly by gravitational settling cannot be measured accurately by standard micrometeorological techniques. In fact, if such large particles are not excluded from detection in some techniques, erroneous results might be obtained.

Some micrometeorological methods can be identified as possibly worthy for development for use in monitoring. They are the variance method, the eddy-accumulation techniques, and the modified Bowen-ratio technique. Others may be indicated as research progresses. For the variance methods, the main limitation seems to be in the ability to find or develop chemical sensors that have fast response (at least 1 Hz) in addition to being linear and having low noise. The other two methods, and others likely to be suggested, rely on accurate mean measurements of concentration differences. Therefore, the following recommendation is made:

*8. Methods to measure dry deposition that depend on concentration differences detected in samples collected in the atmosphere must be supported by chemical/physical analysis methods with standard errors of 1% or less.*

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This recommendation does not necessarily imply that absolute accuracies must be > 1% or less. If the modified Bowen-ratio technique is used, for example, a single sensor might be rigged to alternately measure at two heights. Then the requirement is that the difference, which will usually be 1 to 10% of the mean, be measured accurately. Thus sensor offsets and slow drifts have almost no effect, and errors, say of > 10%, in span calibrations would produce errors of only > 10% in the estimated vertical flux.

Techniques to measure, let alone monitor, fluxes of species associated with acid deposition are presently deficient. Many of the reasons have already been given in this section. There is an urgent need to develop methods with the required accuracy in measuring amounts of strong acids and species such as $H_2SO_4$, $HNO_3$, $SO_4^{=}$, $NO_3^{-}$, $NH_4^{+}$, $NH_3$, and organic acids and bases. This need leads to the following recommendation:

*9. Present capabilities to measure dry deposition for parameterization studies as well as for monitoring must be improved in order to support the acid deposition programs of EPA.*

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## SECTION 5

## CRITIQUE OF METHODS

This section presents brief descriptions and evaluations of various experimental methods for investigating and estimating dry deposition. The methods are representative of most research to date, and include some especially promising techniques. Purely theoretical efforts are not considered separately, but this practice is not meant to imply that such work is unimportant. In fact, all of the experimental methods are directed to some extent towards developing better theories on deposition; the parameterization studies to be considered are specifically concerned with theoretical and semi-empirical expressions of processes that affect deposition.

The main focus is on methods capable of determining dry-deposition rates of various pollutants either by measurement alone or by a combination of measurements with numerical simulations. The methods are sorted into three categories: (A) estimates of accumulation, (B) flux monitoring, and (C) flux parameterization. These distinctions are somewhat artificial; the categories only reflect the intent of the methods as they are currently reported in the scientific literature. A list of the methods is given in Table 1.

If the total accumulation of certain pollutants on a given area could be measured directly, the answers most desired might be found without further effort. This approach constitutes the first category, (A) estimates of accumulation. Periods of time ranging from months to years are usually considered; short-term variations cannot be identified. While areas ranging in size from the entire surface of the earth to individual roughness elements can be addressed in principle, a more practical size is that of individual watersheds characteristically from 1 to 100 km in horizontal dimension. The methods of estimating accumulation could potentially be used for routine monitoring, but the effort required would probably be too large.

Numerous attempts have been made to monitor dry deposition, i.e., to measure fluxes directly on a routine basis. These techniques usually involve sampling at individual points; they are considered in the second category, (B) flux monitoring. Single measurements typically last from hours to weeks, and so shorter-term variations are usually not detected. Ideally, the point measurements are taken over a well-defined surface, e.g., one of uniform vegetation. Actually, all of the point- and areal-sampling field methods listed in this section are potential monitoring techniques, but those listed in category B are the ones that to date have been used most often for monitoring.

TABLE 1. SUMMARY OF METHODS GIVEN IN SECTION 5 TO MEASURE DRY DEPOSITION
(Only those methods for particles that are not affected by gravitational settling are considered.)

| Category | Method | Pollutant | | Monitoring Potential | Research Potential |
|---|---|---|---|---|---|
| | | Particles(P) | Gases(G) | | |
| A. Estimates of Accumulation | Atmospheric radioactivity | P | | low[a] | medium[b] |
| | Mass-balance studies | P | G | low[a] | high[c] |
| B. Flux Monitoring | Open pots | P | | low[d] | low[b,d] |
| | Flat filters | P | | low[d] | low[b,d] |
| | Flat plates and shallow pans | P | | low[d] | low[b,d,q] |
| | Fiber filters | P | | low[d] | low[b,d] |
| | Sticky films | P | | low[d] | low[b,d] |
| C. Flux Parameterization | | | | | |
| 1. Field work | | | | | |
| a. Large areas | Box-budget studies | P | G | low[a] | medium[e] |
| | Airborne eddy correlation | P | G | low[a] | high[f,g] |
| b. Small areas | Gradient | P | G | low[h] | high[i] |
| | Modified Bowen ratio | P | G | high | high[i,j,k] |
| | Eddy correlation | P | G | low[h] | high[f] |
| | Variance | P | G | high | high[f,i,j] |
| | Tracer experiments | P | G | low[a] | medium[l] |
| | Eddy accumulation | P | G | high | high[i] |
| | Leaf washing | P | G | medium[a] | medium[m] |
| | Surface snow sampling | P | G | medium[n] | medium[n] |
| 2. Laboratory | Chamber studies | | G | low | high[o] |
| | Wind-tunnel studies | P | G | low | high[p] |

[a]large effort required
[b]poor particle size discrimination
[c]addresses fate of pollutants to some extent, does not discriminate between particles and gases
[d]easy to collect sample but diffficult to interpret, contamination by gases possible
[e]difficult to achieve the absolute accuracies required
[f]requires fast-response instrumentation
[g]only pollutant tried so far has been ozone
[h]instrumentation difficult to maintain
[i]susceptible to contamination by resuspension of particles
[j]not yet tried for pollutants
[k]requires small short-term drift of sensors
[l]data difficult to interpret
[m]leaf-to-feaf variability is large
[n]works only for light winds, subfreezing temperatures
[o]used mostly to identify important processes
[p]levels of turbulence found in the field difficult to achieve realistically
[q]see alternative viewpoint by Davidson and Lindberg, Appendix C

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The last, and largest, category of purpose to consider is (C) flux parameterization. Many of the field methods listed may become useful for routine monitoring as technology develops; at present, however, these methods in Category C, as opposed to those in Category B, are used primarily for understanding and parameterizing deposition processes. With successful parameterizations, concentrations measured directly or computed in numerical models can be utilized to calculate the vertical fluxes. Category C is further divided into two subcategories according to whether the work is performed in the field or in the laboratory. For field work, both large areas of 1 to 100 km in horizontal extent and small areas of uniform surface characteristics are considered. Sampling times vary from 10 minutes to several days. During short-term studies over small areas, great effort usually must be made to obtain sufficient information on the physical, chemical, and biological characteristics of the surface. For laboratory work, sampling periods are highly variable, but usually short. The type of laboratory observations considered here is concerned with bulk exchange processes in rather large enclosures.

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## A. ESTIMATES OF ACCUMULATION

### ATMOSPHERIC RADIOACTIVITY AS A TRACER FOR PARTICLES

History. Radioactive fallout has been used in many studies of the particle flux to natural surfaces. Some of these studies have addressed the flux into closed ecosystems, such as Crater Lake (see references), by using fallout radioactivity as a tracer "of opportunity".

Usual method of use. Concentrations in air of a selected radioactive material are compared with like concentrations in water bodies or in vegetation, e.g., in order to evaluate the rate of input of the material in question. Sometimes isotope ratios are used to minimize uncertainties about sampling. The method is used to give data regarding small-particle uptake in most applications.

Advantages. This method allows the net uptake rates of well-defined ecosystems to be evaluated with confidence, from relatively simple measurements of vegetation, soil, water, or sediments. Long-term integrations are possible.

Disadvantages. In general, detailed investigation of specific processes is not possible, i.e., diurnal and often seasonal variations cannot be assessed. The role of surface characteristics can be addressed only if they remain constant for long periods of time. In most applications, it is difficult to differentiate between dry and wet deposition contributions. Deposition of background radioactivity and pollutant particles are likely to be similar only if they possess similar size distributions and tropospheric distribution patterns.

Conclusions. The ability to derive net fluxes of small particles is a feature that will continue to be attractive. It seems likely that many other techniques will be tested by comparison with radioactivity data, and it is possible that radioactive fallout might eventually provide the only direct measurement of the small deposition velocities that are expected by some researchers to be characteristic of transfer to smooth surfaces such as large water bodies.

Recommendations. The use of background radioactivity should be more thoroughly investigated to determine its suitability as a monitoring method for particle dry deposition. Experiments using natural radionuclides such as $^{7}Be$ and $^{210}Pb$ should be considered and encouraged. During such studies, meteorological data on winds, temperatures, and humidities should also be collected.

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Small, S. H. (1960) Wet and dry deposition of fallout materials at Kjeller, Tellus, 12, 308-315.

Volchok, H. L., M. Feiner, H. J. Simpson, W. S. Broecker, V. E. Noshkin, V. T. Bowen, and E. Willis. (1970) Ocean fallout -- the Crater Lake experiment. J. Geophys. Res., 75, 1084-1091.

## MASS BALANCE STUDIES FOR PARTICLES AND GASES

History. This method was developed largely by ecologists studying the flowrate of nutrient elements, usually sulfur (S) and nitrogen (N) into and out of agricultural plots and forests. In North America, watersheds are being studied in Tennessee, New York, and New Hampshire.

Usual method of use. In watersheds, a budget model is formulated to account for the outflow (e.g., runoff) and sources (e.g., dry deposition, wet deposition, weathering). Areas affected by chemical fertilizers are usually not used. Typically, measurements can be made to obtain values for all important processes except dry deposition, which is inferred by difference. In controlled fumigation studies, the number of variables to be monitored can be drastically reduced.

Advantages. The net deposition, often for a large area, is inferred. Ecological effects are intensively monitored.

Disadvantages. To infer dry deposition, all other important inflow and outflow rates must be evaluated. Dry deposition is not measured directly but is inferred, and sufficient accuracy is difficult to achieve because the result is often a small difference between large numbers. Some translocation processes must be understood. Chemical species (e.g., sulfate, nitrate, ammonium) may participate in biochemical and geochemical reactions to yield products not considered but that may cause the budget results to be in error. It might not be possible to consider gaseous and particulate deposition separately. Surface characteristics in some studies can be considered only on a long-term areal average.

Conclusions. The approach is not a direct method for measuring dry deposition, but finds fluxes indirectly. However, the method is extremely attractive because it can integrate a large area and the ecological effects usually are intensively monitored.

Recommendations. The continued use of this method should be encouraged especially for watershed and other rather large areas. Careful work should be performed to ensure that significant paths for S and N compounds are not overlooked. Supporting meterological measurements should include winds, temperature, and humidities.

References:

Eaton, J. S., and G. E. Likens. (1978) The imput of gaseous and particulate sulfur to a forest ecosystem. Tellus, 30, 546-551.

Sprugel, D. S., and J. E. Miller. (1979) A field estimate of $SO_2$ deposition velocity to rapidly growing soybeans. Water, Air, and Soil Pollution, 12, 233-236.

## B. FLUX MONITORING

### OPEN POTS FOR PARTICLES

History. Exposed pots were used to measure "total deposition" in early studies of radioactive fallout and are still in use today. Recently, "dry-only" devices that cover themselves automatically when it rains have been developed. They were popularized with the development and subsequent frequent use of the so-called HASL wet-dry collector and a variety of similar devices. Much early work used pots to provide an indication of the maximum amount of material that could be deposited; to this end they were variously covered with sticky material on internal surfaces (see STICKY FILMS) or contained distilled water to retain deposited particles. These days, bare stainless steel or plastic containers are normally employed.

Usual method of use. Identical containers, usually of about 30 cm diameter, are normally mounted side-by-side at heights of about one meter, in areas away from the influence of vegetation, buildings, etc. A rain-sensitive mechanism is used to alternately cover the dry collector when it rains, and the wet collector when it doesn't. These devices are now available from a commercial source, at a cost of about $1500 each. Samples are normally collected over periods of one week to three months.

Advantages. These devices have been selected by the National Atmospheric Deposition Program for use in their standard collection procedures. Recommended exposure, collection, and analysis procedures have been specified. Data obtained at different stations can therefore be compared with some confidence.

Disadvantages. While these collectors might collect in a representative fashion large particles that stick to all surfaces, it is very unlikely that they will provide a surrogate that allows accurate simulation of the complex physical interactions between natural surfaces and fine particles in the naturally-occuring turbulent flow. For example, it has been suggested that for fine particles the outside surface of the pots be used as the collecting area rather than the inside, but in fact the outside, or any other simple artificial surface, is probably inadequate. Also, such collectors might be contaminated by particles resuspended locally. Determination of whether compounds arrived in large or small particles might be confounded by attachment of large to small particles. Reactions of gaseous pollutants with particles already stuck to the surface might contaminate the particulate sample.

Conclusions. Quantification of the surface flux would appear to be in considerable doubt, but identification of the chemical species involved seems possible, even though it will be strongly weighted to the larger particles. Contamination of particles by trace gases appears possible, much as artifact sulfate is generated on some filters. Since the open pot method is a simple and standard method, its use appears to be defensible. Care should be taken to avoid reliance on the "fluxes" estimated from such data, because the relationship to dry deposition of fine aerosols to natural surfaces is not sufficiently known.

Recommendations. This type of sampling is not recommended to monitor dry deposition. Use should probably be continued at sites now established, but future reliance and increased use is not recommended. At the stations where such samplers are now operated, continued use may serve to indicate long-term trends of coarse aerosols. The procedures and effective surface areas assumed should be the same for all pots, following the HASL collectors.

References:

Krey, P. W., and L. E. Toonkel. (1977) Scavenging ratios. Proc. Symp. on Precipitation Scavenging, Champaign, IL, October 14-18, 1974. U.S. Energy Research and Development Agency Symposium Series, 41, 61-70.

Volchok, H. L., and R. T. Graveson. (1975) Wet/dry fallout collection. Proc. of the Second Federal Conf. on the Great Lakes. Interagency Commission on Marine Science and Engineering, Argonne National Laboratory, Argonne, IL, pp. 259-264.

FLAT FILTERS FOR PARTICLES

History. Several notable studies have been conducted in the United States, England, and elsewhere by use of a horizontal sheet of filter paper. Since certain elements are usually associated with specific size ranges of particles, the studies often make use of rather thorough chemical analyses to infer the dependence of deposition velocity on particle size. Estimates of deposition velocities for submicron particles are usually in the range 0.1 to 0.5 cm $s^{-1}$. This method has been used in both the field and the laboratory.

Usual method of use. A nearly square piece of Whatman (541) filter paper about 25 cm on a side is placed horizontally and either covered during rain or placed permanently beneath a rain shield. High-volume samplers are used at the same time to measure total airborne particulate concentrations. Sampling periods are at least several days at each location.

Advantages. A long-term integrated sample is obtained. Many different elements can be considered by analyses in the laboratory. Operation in the field is very simple and inexpensive. The collector might be a slightly more realistic surface for fine aerosols than open pots.

Disadvantages. This method has not been fully standardized and appears to be less popular in the United States than the open-pot HASL collector. Resuspension from the surface is potentially a serious problem. As with open pots (see OPEN POTS), this surface does not accurately simulate the varied surfaces of the natural surroundings; in most cases, too few particles, large and small, will be collected. Attachment of small to large particles may disrupt the relationships expected between chemical species and effective particle size range. Reactions of gases with particles collected may contaminate the samples.

Conclusions. The use of filter paper is not significantly superior to the open-pot method because of the overwhelming failure to simulate natural surfaces.

Recommendations. This technique is not recommended as a dry-deposition monitoring method. Attempts at improving this technique will probably not be highly beneficial.

References:

Muhlbaer, J. L. (1978) The chemistry of precipitation near the Chalk Point River plant. Ph.D. Thesis, University of Maryland, College Park, MD. 322 pp.

Peirson, D. H., P. A. Cawse, and R. S. Cambray. (1974) Chemical uniformity of airborne particulate material, and a maritime effect. Nature, 251, 675-679.

## FLAT PLATES AND SHALLOW PANS FOR PARTICLES

History. Various types of horizontal plates, with and without rims, were used in many early studies of particle deposition. It was recognized that these simple devices provided imprecise indications of the rate at which particles were being delivered to natural surfaces, but nevertheless their use was wide-spread. Some tests indicated that particles deposited on the sampling surface could be more efficiently retained if the surface were modified by covering it with adhesive, gauze, or water. In some experiments, deposition substrates were specially selected to have desirable chemical characteristics.

Usual method of use. The devices are usually placed at heights of one meter, with samples being collected at intervals from several days to months. Rainfall presents an obvious difficulty. The material deposited is analyzed by standard chemical techniques.

Advantages. Samples are collected easily and the system can be operated by relatively untrained personnel. A long-term sample is obtained. Many different chemical species can be investigated.

Disadvantages. Techniques have not been standardized. As with similar methods, simulation of actual natural surfaces and their interaction with atmospheric turbulence is very difficult. Attachment of small particles to larger ones may disrupt the relationships expected between chemical species and effective particle size ranges. Reactions of gases with particles collected may contaminate the samples. If water is placed in pan collectors, gas transfer can be a dominating factor for some pollutants (e.g., sulfur).

Conclusions. As with the use of all surrogate-surface systems, the analogy with the natural case is rather poor and causes considerable doubt about how results should be interpreted.

Recommendations. This type of approach is not recommended as a dry-deposition monitoring method. Future improvements probably would not be adequate. (An alternative viewpoint is presented by Davidson and Lindberg in Appendix C.)

References:

Islitzer, N. F., and R. K. Dumbaulk. (1963) Atmospheric diffusion-deposition studies over flat terrain. Inter. J. Air and Water Pollut., 7, 999-1022.

Markee, E. H. Jr. (1967) Turbulent transfer characteristics of radioactive effluents from air to grass. Proc. U.S. Atomic Energy Commission Meteorological Information Meeting, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada, Sept. 11-14, 1967, Atomic Energy of Canada Limited Report AECL-2787, 589-601.

Davidson, C. I. (1977) The deposition of trace metal containing particles in the Los Angles Basin. J. Powder Technol., 18, 117-126.

FIBER FILTER: FOR PARTICLES AND GASES

History. The use of fiber filter mats was an attempt to avoid the problems of resuspension for coarse particles and the low deposition rates for fine aerosols that are present when using flat plates.

Usual method of use. Fiber filter mats are placed in vegetative canopies in such a manner that leaves do not shield them, and so that they are not subjected to avian interferences. After exposure for one to two weeks, the filters are removed for mass and chemical analysis. For gas sampling, the filters are coated with an active chemical.

Advantages. Sampling is easy to perform and is inexpensive. A wide range of chemical species can be investigated.

Disadvantages. The surface resistance of the fiber filter mats does not match that of the vegetation. Also, the fiber filters (especially when glass) may be biased due to unrepresentative gas-phase reactions on its surface.

Conclusions. The surrogate-surface does not represent the behavior of natural vegetation. Interpretations of data are difficult. The method is not acceptable as a dry deposition monitoring technique.

Recommendations. The method should not be encouraged and efforts to further develop it as a method to monitor dry deposition are not warranted.

References:

Israel, A. W. (1977) Differences in the accumulation of gaseous and particulate fluorine compounds by forage vegetation and lined filter paper samplers. Atmos. Environ., 11, 183-188.

Tomingus, R., and G. Voltmer. (1978) Abscheidung von Benz(a)pyren aus der Atmosphaere auf Glasfaserfiltern (Deposition of benzo(a)pyrene from the atmosphere onto glass fiber filters). Staub-Reinhalt Luft, 38, 216.

## STICKY FILMS FOR PARTICLES

History. Sticky surfaces have been used in a variety of configurations to collect different kinds of particles. For example, glass slides have been coated with petroleum jelly or with glycerin to collect spores. Adhesive-coated acetate films were used in the routine monitoring of radioactive fallout during the 1950's and 60's. Workers of the Union of Soviet Socialist Republics employed flat steel plates and collection vessels of various geometries that were sometimes coated with glycerin on the collection surfaces. In a variation on the more common method, some USSR workers employed gauze as a collection method instead of a sticky substance.

Usual method of use. For the radioactive fallout studies, a flat horizontal surface was usually mounted at heights of one meter, well away from vegetation and preferably somehow protected from birds. The exposed surface was coated with an adhesive substance, which was sometimes similar to flypaper in consistency but was often some sort of grease. Surfaces were exposed in all weather conditions. In the fallout studies, exposure times varied from one day to several weeks. The devices were "calibrated" in terms of the total (wet plus dry) deposition against the accumulation to soil and results obtained using open pots.

Advantages. Obvious advantages include simplicity and lack of expense. The technique is easily mastered by relatively untrained personnel, and analysis can be as complicated as one likes to make it.

Disadvantages. It seems fairly clear that devices of this kind will provide a measure of what is in the air, but the relationship of the deposition to the underlying surface is not obvious, especially when resuspension or surface emissions are suspected of playing a role in the net transfer. Early work (HASL-42a, 1958) indicated that the relationship between gummed film deposits and collections in open pots was not constant. Chemical speciation of deposited material is likely to prove difficult.

Recommendations. These methods are already largely obsolete. They should not receive further encouragement, nor should efforts be made to improve them.

References:

HASL-42a. (1958) Environmental Contamination from Weapons Tests. U.S. Atomic Energy Commission, Health and Safety Laboratory, New York, NY. E. P. Hardy Jr. and J. H. Harley (eds.). 95 pp.

Aleksandrov, N. N., B. B. Goroshko, V. G. Kovalenko, and F. A. Panfilova. (1965) Influence of the meteorological conditions on the collection efficiency of radioactive contaminants. In: Radioactive Isotopes in the Atmosphere and Their Use in Meteorology, translation of material presented at the Conference on Nuclear Technology, Obninsk, U.S.S.R., 3 - 6 February, 1964; Index to Scientific and Technical Proceedings Catalog Number 1801, pp. 354-359.

**Eisenbud, M., and J. H. Harley. (1955) Radioactive fallout in the United States. Science, 123, 677-680.**



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## C. FLUX PARAMETERIZATION

### 1. FIELD WORK

#### a. LARGE AREAS

**BOX-BUDGET STUDIES FOR PARTICLES AND GASES**

History. One of the oldest methods of studying atmospheric fluxes is to evaluate inflow and outflow associated with a particular region during part of a day and then to estimate the surface deposition from the difference and details of inputs within the region. A similar approach is to measure changes of concentration in a Lagrangian sense, with the mean flow of air over the area studied. Such measurements over Great Britain have resulted in a convincing evaluation of the average deposition velocity for $SO_2$.

Usual method of use. In most studies, a spatially-uniform area is selected and concentration profiles are documented at upwind and downwind edges. These profiles are then coupled with equally detailed wind profiles to evaluate the net source or sink term within the region.

Advantages. The net surface flux over the area in question is evaluated independently without the need for detailed knowledge of conditions in the atmospheric surface layer.

Disadvantages. Deposition estimates are subject to large errors because very small differences are found. Usually, travel distances of the order of 100 km or more are needed in order for horizontal flux differences to exceed a few percent even for actively exchanged pollutants. Wind and concentration profiles need to be extended above the height at which pollutants mix. In practice, during the daytime heights to above 2 km must often be considered, which usually requires the use of aircraft. Crosswind uniformity in the flow field, the surface vegetation, and the topography must be sufficient to ensure negligible "leakage" through the "sides" of the "box". Anthropogenic sources within the region must be well known. Because of the large areas and rather long sampling periods required, the capacity to investigate diurnal variations and the effects of specific surfaces is quite limited. Chemical reactions involving the pollutant of interest must either be assumed to be insignificant or accounted for in a sufficiently accurate manner.

Conclusions. Although this method is outwardly attractive, the experimental constraints associated with it are extremely demanding.

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Recommendations. This experimental method is too expensive and difficult to be suitable for monitoring directly. For verification of numerical models and for testing of parameterizations over complex terrain, however, improvements of aircraft instruments and remote-sensor capabilities should be encouraged in order to provide better estimates of dry deposition over scales of approximately 100 km.

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AIRBORNE EDDY CORRELATION FOR PARTICLES AND GASES

History. Airborne gust probes have been developed over the last twenty years to measure the three eddy components of atmospheric motion ($u'$, $v'$, $w'$). Linking gyroscopes or an inertial navigation system (INS) with a gust probe provided the means to remove effects of motions of the aircraft platform. Additions of temperature and water vapor sensors provided the capability to measure sensible and latent heat fluxes, in addition to the momentum fluxes. Applications in boundary layer meteorology have been extensive. Recently, new pollutant sensors, potentially suitable for coupling with the gust probe so as to measure fluxes, have been or are being developed for trace gases (e.g., $O_3$) and small particles.

Usual method of use. Rapid-response (~10Hz) vanes and a pitot tube are used to measure the wind components. An INS and electronic filtering remove aircraft motion and noise. Other rapid-response sensors detect the concentration of the atmospheric constituents of interest. Flux measurements are made in straight, horizontal flight and altitudes and, in patterns that suit the application. Instantaneous and mean fluxes, and corresponding spectral analyses are produced.

Advantages. Aircraft survey large areas in a very short time; they permit crosswind and along-wind flux measurements, whereas towers only see the latter aspect of transport and require much longer time periods to do so. Deposition velocities over various types of complex terrain can be studied. Flight altitudes can be as low as 10 m for direct measurements of flux to the surface. Multiple altitude measurements for budget studies, and higher level measurements of, e.g., fluxes through cumulus clouds (boundary layer venting), are feasible.

Disadvantages. Pollutant sensors sufficiently fast in response are extremely difficult to construct. Effects of decoupling and of flux divergence between the lowest flight level and the surface, as in nocturnal stable air, must be determined for surface deposition studies. Over complex terrain, interpretation of observations could require sophisticated modeling; detailed knowledge of surface characteristics under the flight paths is needed (but is obtainable). The technical complexity restricts uses to research. Operational costs are high, and although logistically feasible, aircraft are normally not operated on station continuously.

Conclusions. The airborne eddy-correlation method is intended for research rather than routine monitoring of dry deposition. The method can provide accurate measurements of vertical and horizontal fluxes at flight level. Measurements from the aircraft and towers are complementary in many ways; primarily, towers provide near-surface reference/calibration measurement for the aircraft and help to evaluate changes of flux with height, whereas the aircraft covers large areas not observable with stationary point systems.

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Recommendations. The use of this method, in conjunction with an extensive characterization of underlying natural surfaces and complementary eddy-correlation or other measurements near the ground, may become the best approach to parameterizing deposition. For this method to measure fluxes of acidic gases and aerosols, fast-response pollutant analyzers must be developed that can be operated in aircraft. A rapid-response ozone sensor has been used with the gust probe in recent EPA field studies; improvement of this sensor is in progress. Other suitable gas and particle sensors are not yet available, although some development is underway.

Further exploration of the airborne eddy-correlation method is recommended. Additional studies over complex terrain, with emphasis on atmospheric deposition, should be attempted. Since planetary boundary layer structures can control the amount of pollutant delivered to the surface at certain times, aircraft measurements throughout the depth of the boundary layer should be performed occasionally. In initial studies, comparison with measurements on towers should be conducted in uniform terrain. The measurements of momentum, sensible heat, and water vapor flux should be obtained as well, since they are required to parameterize surface uptake and boundary-layer structure.

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C. FLUX PARAMETERIZATION
1. FIELD WORK
b. SMALL AREAS

GRADIENTS FOR GASES AND PARTICLES

History. Studies of the relationships of fluxes to gradients in the atmospheric surface layer have led to formulations for eddy diffusivities that can be applied to differences in pollutant concentration measured between two or more heights. This method gained favor among air-pollution meteorologists following early work to address sulfur dioxide and ozone fluxes. Initial uncertainty about the way to estimate an appropriate eddy diffusivity, whether as heat or momentum, has now been resolved in favor of the former.

Usual method of use. Concentration differences between two or more levels within about 10 m above a natural, flat, and spatially-homogeneous surface are used to evaluate a local gradient that is then taken to be representative of the area as a whole. Eddy diffusivities are evaluated as a function of momentum flux, surface roughness, and atmospheric stability, which are derived from supporting meteorological data obtained nearby.

Advantages. Fast-response sensors are not needed. Interpretation of gradients is conceptually straightforward and has received a good deal of attention as a result. The information needed to determine eddy diffusivity provides directly several of the parameters needed to infer some of the processes that control deposition at the surface.

Disadvantages. The familiar arguments on the required fetch apply with considerable force, since local surface inhomogeneities will not only influence pollutant profiles directly but will also affect the diffusivities that need to be applied to them. Artificial sources close upwind cannot be tolerated. Concentration differences are likely to be exceedingly small; in most circumstances vertical differences of about 1% in concentration will need to be measured over a two-fold height interval. To measure the small differences, it is usually necessary to allow each sensor to measure at several heights so that systematic differences between sensors are eliminated; sampling over longer time intervals is usually necessary. With particles, surface (re)suspension and (re)emission can cause concentrations to increase near a natural surface, even though a downward flux continues. The fluxes measured do not include components associated with gravitational settling. This method often fails over tall vegetation because of the difficulties of estimating eddy diffusivities, and because gradients are exceedingly small.

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Conclusions. Many gradient studies have failed to recognize either the need for micrometeorological criteria to be satisfied or the requirement for exceedingly accurate measurements of concentration differences. Nevertheless, the work provides an opportunity to investigate the flux of pollutants for which the only sensors available are slow in response.

Recommendations. This technique is a useful parameterization tool for surfaces with short or no vegetation. The need to estimate diffusivity as a function of height makes this method less attractive than others (e.g., see MODIFIED BOWEN RATIO) as a monitoring technique.

References:

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MODIFIED BOWEN RATIO FOR PARTICLES AND GASES

History. A combination method of Bowen ratio and energy balance is perhaps one of the oldest and most tested methods for obtaining water vapor fluxes. An essential assumption, that eddy diffusivities for heat, water vapor, and, in this case, pollutants are equal, is now accepted with few reservations. Applications to ozone and carbon dioxide have been reported since 1970. This method can be considered a simplified variation of GRADIENTS.

Usual method of use. The pollutant eddy diffusivities are assumed to be the same as for sensible heat or water vapor. The pollutant flux is given by the product of water vapor flux and pollutant concentration difference, divided by the difference in specific humidity. A normalized sensible heat flux and temperature differences can be used in place of the water-vapor variables. Differences must be measured over the same height interval and at the same location. The fluxes of heat or water vapor would ordinarily be obtained by energy-balance Bowen-ratio methods or by eddy correlation.

Advantages. Fluxes are measured without assumptions about the nature of the surface cover. Fast-response chemical sensors are not needed.

Disadvantages. The chemical analyses must be able to detect differences in successive samples of less than 1% (see Hicks and Wesely, 1978). This need for accuracy in differences usually requires periodic interchanging of sensor sampling points, which results in the need for sampling times of at least one hour to obtain a meaningful average. The energy-balance Bowen-ratio method has certain difficulties of its own: (1) soil heat flux or canopy heat storage must be estimated, especially near sunrise and sunset; (2) temperature differences cannot be found accurately in near-neutral conditions; (3) routine measurement of differences in water vapor content can be difficult. With particles, fluxes due to gravitational settling are not detected and (re)suspension of large particles can invalidate the results. Measurements should be well above tall vegetations, which often requires excessive fetches.

Conclusions. A major limitation is the demand for precision of sample analysis. The equipment maintenance required is less than average for micrometeorological methods, but can still be very demanding.

Recommendation. This method can be very useful for parameterization studies at a well-instrumented, well-maintained site for periods as long as one season. Utilization for routine monitoring should be investigated.

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## EDDY CORRELATION FOR PARTICLES AND GASES

History. United Kingdom workers first applied the covariance method to evaluate the transfer of momentum $\rho\overline{u'w'}$ by painstaking hand-evaluation of chart records of horizontal (u) and vertical (w) wind data. Subsequent efforts extended the method to the cases of sensible heat and water vapor, and recently it has been applied to the measurement of vertical fluxes of a range of trace gases and small particles.

Usual method of use. Sensitive and fast-response anemometers are placed at a height of 1 to 10 m to detect fluctuations in the vertical wind component, w. Adjacent to the anemometry, measurements are made of the concentration of the pollutant of interest, c. Mean values of both signals are removed, to produce signals fluctuating about zero, w' and c'. The product w'c' is then calculated and averaged to produce the turbulent flux of the quantity c. This flux equals that at the surface if stringent fetch/height criteria are met; in general, the height of operation of the sensors needs to be less than 0.5% of the uniform horizontal upwind fetch. At the same time, the sum of exponential response time and delay time of each sensor used should be less than height divided by mean wind speed.

Advantages. Covariance measurements provide absolute evaluations of vertical fluxes in natural circumstances, without the need for assumptions regarding appropriate diffusivities and without making any assumption about the nature of the surface cover.

Disadvantages. Fast-response chemical sensors often need to be developed. In practice, the fetch/height constraints and the increase in the frequency of turbulent transfer mechanisms near the surface combine to require the sum of exponential response time and delay time to be less than about one second. This makes the task extremely demanding, and only a few pollutant fluxes have been measured by this method. Particle flux due to gravitational settling is not detected and significant resuspension of large particles can invalidate results.

Conclusions. Provided the standard micrometeorological criteria are met, this method is capable of providing accurate measurements of surface fluxes.

Recommendations. In parameterization studies, the measurements of momentum, sensible heat, and latent heat flux should be obtained as well as the pollutant flux, since these are required to obtain surface-related information and are relatively easy to obtain. Monitoring capabilities should be assessed.

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VARIANCE FOR PARTICLES AND GASES

History. Experimental studies of turbulence in the atmospheric surface layer in the 1960's and 1970's have shown that turbulent variations of temperature and humidity are highly correlated and can be parameterized in terms of surface layer variables. The accompanying theory of the similarity of heat and water vapor behavior can be extended to trace gases and fine particles, except perhaps in some cases where fluxes are very small. While the variance method has not yet been tried directly, very recent field tests have indicated that the method is feasible.

Usual method of use. The variances of pollutant concentration and of temperature or humidity fluctuations are measured simultaneously at the same height and location. Sensible heat flux (or evaporation) is measured also, so that the pollutant flux can be estimated as the product of the temperature (or humidity) flux times the standard deviation of pollutant concentration, divided by the standard deviation of temperature (or humidity). Rather the standard deviations from total variance, a selected bandpass for variance averaged over periods of 10 min to 1 hr can be used. See MODIFIED BOWEN RATIO for a discussion of means likely to obtain sensible heat flux or evaporation rate.

Advantages. Fluxes can be measured without assumptions about the nature of the surface. Measurements of vertical wind-speed fluctuations might be avoided. As compared to eddy correlation, lag times can be much larger, so that long sample lines can be used for the chemical sensor, and the time-response requirements can be slightly relaxed if a low-frequency band-pass variance is computed.

Disadvantages. Suitable fast-response chemical sensors must be developed. Sensor random noise is a more serious problem here as compared to eddy correlation. If temperature is used, the method will usually fail during near-neutral conditions; if humidity is used, suitable humidity sensors are expensive and difficult to maintain over long periods of time, and the method will fail in dry conditions and often in cold conditions. The direction (up versus down) of the pollutant flux cannot be determined. With particles, fluxes due to gravitational settling are not detected and (re)suspension of large particles can invalidate the results. Measurements should be well above tall vegetative canopies, which results in the usual need for large fetches.

Conclusions. If the pollutant sensor has very low noise levels, this method might be superior to direct eddy correlation. Even if heat or water vapor flux is measured simultaneously by eddy correlation, a variance method might be more feasible than eddy correlation for the pollutant flux because low-frequency band-pass filtering can reduce the requirement for small response and delay times.

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**Recommendations.** This method might be especially attractive for pollutants for which sensors are available that have long delay times and response times only slightly too large for eddy correlation. Of the micrometeorological methods, the variance technique might hold the most promise for monitoring of some pollutants.

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## TRACER EXPERIMENTS FOR PARTICLES AND GASES

History. Studies on the possible effects of inadvertent releases of radioactivity into the atmosphere led to a series of sophisticated field studies involving the release of tagged material such as $^{131}I$ and $^{35}SO_2$ over various natural surfaces. From these studies, a good deal of our present understanding of surface deposition properties was derived. Interest in these methods has continued, even though the use of radioactivity as a tracer material for experiments such as these is now prohibitied in some countries, including the United States.

Usual method of use. Material tagged with some convenient and easily measured tracer is released into air flowing above a vegetated surface from which samples are extracted for analysis. Air concentration measurements are also made. Tracer materials have ranged from radioactive gases to fluorescent particles. Alternative methods include the use of two tracers, one of which is inert, to infer deposition by assessment of depletion of the active tracer over a relatively large area.

Advantages. Studies of the deposition of tagged material from plumes traversing various surfaces address the question of inadvertant pollution release in a direct and easily understandable manner. If the tracer material is carefully chosen, sampling of deposited material can be quite accurate.

Disadvantages. The tracer particle and pollutant particle size distributions may not be the same, which may lead to different removal rates. For both gases and particles at short distances from release points, mixing is insufficient for effective simulation of deposition of pollutants in the planetary boundary layer well downwind from sources, i.e., the turbulent structure of eddies that carry the tracers to the surface may be artificially weighted towards small eddies; vertical gradients are distorted so that concentrations in the air above the surface can be misleading. The dependence of deposition rates on wind speed may be hard to determine because of dilution varying with wind speed and turbulence intensity. Also, surface sampling can be tedious, and the logistical problems of following the plume over long distances can be severe.

Conclusions. Releases of special tracers can be used to develop parameterizations suitable for wider application if care is taken to document local horizontal and vertical concentration gradients. Results from tracers in early studies were quite useful, when alternative methods were few.

Recommendations. Tracer studies can be recommended for the study of deposition processes only if some unique advantage is found. The distribution of tagged pollutants within vegetated canopies could be the subject of a tracer study. Another study worthy of consideration deals with resuspension of radioactive soil particles. When tracers are used in studies of atmospheric dispersion, dry deposition often must be considered anyway; a little extra effort might yield valuable information on deposition processes.

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## EDDY ACCUMULATION FOR PARTICLES AND GASES

History. During the middle 1960's, the eddy-accumulation method was first considered seriously as a possible means of avoiding the need for rapid-response sensors for scalar quantities in eddy correlation. Most often, a simplified instrument for measuring the flux of water vapor was sought. In later considerations, emphasis has been on trace gases, especially pollutants and carbon dioxide. A successful application of this method has not yet been reported.

Usual method of use. See the discussion under EDDY CORRELATION. Fast-response vertical velocity signals are manipulated to control the sampling rates of two separate mean-measurement systems, one associated with updrafts and the other with downdrafts. As with conventional eddy correlation, the anemometer must be well aligned in the vertical, preferably with high-pass filtering applied to the velocity signal as well. The eddy flux is evaluated from the differences in concentrations of the material of interest in air accumulated by the two sampling systems. The usual micrometeorological siting and sampling constraints apply.

Advantages. The technique offers the benefits of a genuine eddy-correlation calculation while sidestepping the need for fast-response pollutant sensing. For some pollutants, analysis could be performed on samples taken to a chemistry laboratory.

Disadvantages. Differences in concentration between the two samples are likely to be small, a few percent or less. Aerosol sampling poses special problems for this technique because inlet sampling efficiency is likely to be a function of particle size, horizontal wind velocity, and inlet velocity. Particle fluxes resulting from gravitational settling should not be detected, but significant local resuspension of large particles can invalidate results.

Conclusions. This method is a suitable technique for investigation of the dependence of dry flux upon micrometeorological and surface variables. The lack of success in past attempts is evidence of the difficulties involved. Nevertheless, active interest persists because of the potential benefits. While the eddy-accumulation approach offers high potential as a dry-deposition monitoring technique, it suffers in at least three aspects: (1) lack of a suitable electromechanical sampling system, (2) variations of sampler inlet efficiency for aerosols, and (3) the need for chemical analysis precision errors to be less than 1%.

Recommendations. Work to develop dry-deposition measurement systems based on the principle of eddy accumulation should be initiated. Monitoring capabilities should be assessed.

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## LEAF WASHING FOR PARTICLES AND GASES

History. The enrichment of pollutants in rainfall as it penetrates foliage is recognized to be a major route by which several elements are delivered to the floor of a forest. Dry deposition between rains can be a major source of the contaminants washed to the ground. Recent studies at Oak Ridge National Laboratory and elsewhere have attempted to quantify this source by measuring the amount of sulfate and certain trace metals that can be rinsed from leaves taken from the canopy, from artificial surfaces placed in the canopy, and from the canopy itself during precipitation.

Usual method of use. Investigations require detailed rain chemistry studies, with collection and analysis of rainfall incident upon a canopy and of simultaneous throughfall arriving at the floor. An obvious innovation is to undertake careful washing of individual leaves, so as to yield measurements of fluxes of particles and, to a lesser extent, gases during prescribed periods. Samples are taken at the beginning as well as at the end of each sample period in order to account for contaminants already present and to estimate the contributions from leaf leachate. Internal foliage sources may also be estimated by comparison of "wash" concentrations from leaves with those from inert surfaces exposed in the canopy during the same sampling period.

Advantages. This method results in direct measurements of deposition. Results obtained for selected foliage samples can be extended to entire canopies by relating deposition representative of height intervals to leaf areas sampled in each interval.

Disadvantages. Because of the great spatial variability in the amount deposited to leaves, a very large number of samples must be taken and analyzed. Leaves can be a highly variable source of some chemical species, which might be mistaken for the consequences of atmospheric deposition. A redistribution of pollutants within the canopy can occur by various means, which can confuse interpretation. Due to the great spatial variability of contaminants in the "throughfall" rain samples (under a canopy), relating deposited material to material washed down naturally might be doubly difficult. This method will not respond reliably to species that may be unstable, e.g., $H_2SO_4$ and $HNO_3$. Nitrates may evaporate and strong acids may be neutralized between rains. Peak doses may be difficult to identify because of the time elapsed between samples for collection of sufficient materials for analysis.

Conclusions. The full benefits of this method have yet to be explored, but for suitable canopies, it offers a means to monitor dry deposition, especially for stable species such as sulfate. Measurements of wind speeds and atmospheric stability should be taken during experiments.

Recommendations. The use of the method should be encouraged, especially for mass-balance experiments in watersheds (see MASS BALANCE STUDIES). Simultaneous experiments on comparing concentrations in rainfall with throughfall must be conducted in order to check results. (This rainfall and

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throughfall method itself will be useful in dry deposition studies if comparisons are successful.)

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SURFACE SNOW SAMPLING FOR PARTICLES AND GASES

History. Only recently have experimental methods been developed to permit snow sampling and analysis for trace contaminants at low concentrations. The methods currently in use have been of primary interest in the Arctic and Antarctic regions, although some work in urban areas has been performed.

Usual method of use. Fresh surface snow is collected immediately following a storm and analyzed for the species of interest, providing baseline values that correspond to the wet deposition rates. After one or more days, the surface snow is again analyzed. The increases in contaminant levels provide a measure of dry deposition onto the snow.

Advantages. When fluxes are small or when winds are very light, this method is more likely to be successful than micrometeorological methods. The sampling of snow provides a simple and direct flux measurement.

Disadvantages. Data interpretation may be difficult. Snow sublimes, causing the pollutant to become more concentrated. Strong acids have freezing points lower than water, and they are known to migrate downward in snow. Since blowing and drifting snow redistributes contaminants and thus makes representative sampling very difficult, this method should probably be used only for periods of light winds.

Conclusions. The method will probably provide useful information under limited ambient conditions and should be applied in certain parameterization studies. Wind speeds and atmospheric stability should be measured concurrently.

Recommendations. Obviously, this method is useful only for snow surfaces. Low winds and temperatures several degrees below freezing are necessary. The method may be helpful for use in certain northern areas, but will require additional research before being implemented.

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## C. FLUX PARAMETERIZATION
### 2. LABORATORY

CHAMBER STUDIES FOR GASES

History. In studies of ecological effects of air pollutants such as $SO_2$ and $O_3$, the use of chambers has become an accepted method, although direct transfer of laboratory results to natural circumstances is quite difficult. Measurement of the flux of pollutants into plants or even into individual leaves is possible, under fairly controlled circumstances. Emphasis often has been on the processes that control deposition, rather than precise quantitative evaluation. The increased use of chambers in the field has improved the quantitative aspects of the experiments.

Usual method of use. Controlled amounts of pollutants are administered in stirred chambers to plants, leaves, or other surfaces. Uptake is determined by measurements of differences in concentrations in outflow versus inflow, by the rate of change of concentration with time in the chamber, or by measurement of uptake of radioactive substances. This method can be applied to vegetation or other types of surfaces, such as soils.

Advantages. The roles of individual biological or chemical factors can be examined in considerable detail. Relative evaluation of deposition rates for different types of surfaces can be obtained quickly. The method can make use of chamber equipment that is often developed in conjunction with related investigations of ecological impacts.

Disadvantages. Realistic conditions are difficult to achieve. Vegetation in the laboratory, for example, is quite different from vegetation grown in the field, because of decreased light levels. Since turbulence conditions in the field cannot be truly simulated in chambers, inaccurate results are obtained if aerodynamic resistances are important relative to surface resistances. Relatively limited information is obtained on procedures to add up transfer to individual surface elements in order to obtain the total deposition from the atmosphere.

Conclusions. There are many different types of chamber techniques, some of which contain aspects of small wind tunnels. Chamber methods provide an important way to investigate the relative effects of biological or chemical factors on the surface resistance to gaseous pollutant fluxes.

Recommendations. There is no obvious manner in which chambers can be used to monitor fluxes routinely. It is essential that parameterization studies involving chambers be continued.

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WIND-TUNNEL STUDIES FOR PARTICLES AND GASES

History. Many formative studies of pollutant interactions with surfaces have been conducted in wind tunnels, primarily in Europe and later in the United States. These studies tended to approach the problem in a reductionist manner, by investigation of selected gaseous species and types of particles deposited to artificial surfaces of various kinds. The work has been expanded to address the case of live vegetation and water surfaces. Much of our present understanding of the manner in which surface properties influence dry deposition has been attained by use of wind tunnels.

Usual method of use. Selected pollutants are "tagged" in some way (often by use of radioactivity or some fluorescent material) and injected into wind-tunnel flow above a surface of particular interest. Surface materials are then sampled to determine uptake rates. Concentrations are usually measured very close to the surface, within the lowest few centimeters, in order to maximize effective fetch/height ratios.

Advantages. Detailed studies are possible of deposition velocities of particles and gases to surfaces. The effects of varying wind speed, chemical characteristics of gases, particle size, surface roughness element configuration, etc. can be investigated.

Disadvantages. Particles used are sometimes not similar to those normally found in nature, not only because of the size distribution but also because of chemical characteristics. Only small vegetation can be considered since tunnels are limited in size. The fetches available are clearly constrained. Samples of vegetation grown indoors can differ appreciably from those grown in the field. The extreme gustiness characteristic of turbulence in the atmospheric surface layer during unstable conditions cannot be reproduced. Water surface effects may not be adequately reproduced in wind tunnels, giving rise to doubts about the accuracy of particle deposition measurements to bodies of water.

Conclusions. Deposition processes can be closely scrutinized by wind tunnel experiments, but great care needs to be exercised that the experimental set-up satisfies the theoretical requirements, especially regarding the nature of the surface used, characteristics of turbulence, and the available fetch/height ratio.

Recommendations. Wind tunnel studies offer a unique opportunity to test the relative importance of different surface mechanisms that potentially contribute to the process of dry deposition. Studies of the roles of factors such as wetness, microscale roughness, stickiness, and electrostatic characterics should be increased.

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## SECTION 6

## INDIRECT CALCULATION OF DEPOSITION RATES

Another method for determining deposition is always implied to some extent when parameterization is discussed. This more indirect method is the application of parameterizations to measurements of pollutant concentrations and a few selected companion variables in order to compute the dry deposition rates indirectly. The use of concentrations monitored at a network of stations is emphasized here, but concentrations computed by numerical models is inherently considered also. The following description summarizes this method.

### CONCENTRATION MONITORING AND INTERPRETATION FOR PARTICLES AND GASES

History. For airborne particulate and gaseous pollutants, there is no historical data base on dry deposition except for some exceptional cases such as architectural surfaces. However, there are data bases on air quality and there are networks for measuring air quality in operation at the present time. Thus, an approach to monitoring dry deposition is to use the measurements of air-pollutant concentrations at a single height and employ parameterizations of dry deposition to yield the deposition rates.

Method of use. At one height above a well-specified, uniform surface typical of the area, pollutant concentrations are measured and typically averaged over one-hour intervals. From micrometeorological observations and knowledge of surface behavior, deposition velocities are inferred. Pollutant flux is obtained as the product of deposition velocity and concentration. Companion variables that form the basis for the meteorological calculations are wind speed, atmospheric stability, and surface roughness; depending on pollutant and surface characteristics, a range of other properties must be monitored.

Advantages. Monitoring stations are already in place for some pollutants. Other types of observations are minimized.

Disadvantages. Single-height concentration monitoring is fundamentally deficient. Meteorological information alone will not yield a measurement of deposition velocity because it cannot account for all surface variables, such as the physiology of vegetation. Thus, careful observations of surface characteristics must be made. While it is probably not essential that the concentrations be measured at extremely uniform sites, micrometeorological measurements should be. The alternative, less exact but more practical method is to infer atmospheric variables from standard meteorological measurements and assume diurnal cycles of stability.

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Conclusions. Dry deposition is not actually monitored. The development of accurate parameterizations is crucial. In many cases, empirical correlations between the gross aspects of the physical environment and surface conditions must be estimated in order to supply the parameters needed. For example, the resistance to gas uptake through stomata of plant leaves can be approximated according to atmospheric stability categories.

Recommendations. Until reliable methods suitable for directly monitoring dry deposition are developed, use of monitored concentrations may be the only alternative that is practical yet sufficiently accurate. Parameterizations of $SO_2$ and $O_3$ fluxes to many surfaces are already available, but are not well founded for submicron particles and many gases. For surfaces, additional work above tall plant canopies such as forests is needed.

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## SOME RESEARCH NEEDS

An attempt is made here to describe some of the processes controlling dry deposition that need to be better understood, and to suggest methods of research that might be employed. These considerations complement the discussions on parameterization procedures presented earlier in Section 5. The major problem in parameterizing the flux of specified pollution species to a given surface can often be identified by noting where the resistance to vertical transport is greatest. For example, uptakes of certain gases by vegetation is mainly controlled by the sizes of the leaf stomatal openings. For submicron particles, deposition to smooth inert surfaces is limited by the slow diffusion through the quasi-laminar layer of air closest to the surface; any means of effectively short-circuiting that resistance can result in large changes in deposition rates.

Practical considerations limit the number of chemical species and types of surfaces that can be investigated. The surfaces chosen for study usually should be those most prevalent or characteristic of the area or region considered. At a minimum, the pollutants to be examined should be the criteria pollutants and particles in many small size intervals, with emphasis on submicron diameters. Of course, studies are aided by grouping together pollutants with similar chemical and physical properties. Categories might depend on solubility in water or reactivity with various substrates, for example. For particles, the processes of diffusion, impaction, and sedimentation can sometimes be studied separately, but care must be taken because these are smooth functions of particle size in overlapping size ranges.

Table 2 summarizes identified research needs, grouped according to scales of the phenomena of interest and correlated with experimental methods of investigation given in Table 1. The smallest scale sizes, those associated with $r_e$ in Table 2, are often best studied in the laboratory, where, for example, reactivity with various substrates can be examined. Further work on particle deposition is needed to determine the effects of surface stickiness and microscale roughness. Continued work on diffusiophoresis, thermophoresis, and electrophoresis is needed, but with greater emphasis on the environmental conditions that exist in the field. For example, electrical charges on particles vary with the "age" of the aerosol, resulting in varying effects of electrophoresis on deposition. Another problem is that pollutants are often (re)suspended or (re)emitted, due to a variety of causes that are often not appreciated until what appears as anomolous results are found in laboratory and field experiments. Small-scale surface phenomena that need to be studied in this respect include decomposition of organic material and chemical reactions at surfaces that "recycle" pollutants.

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TABLE 2. SUMMARY OF RESEARCH PRESENTLY NEEDED ON DRY DEPOSITION PROCESSES

| Contributing Process (resistance) | Length, Scale or Height (m) | Topics of Concern | Recommended Methods of Experimental Research |
|---|---|---|---|
| $r_e$, resistance of individual surface elements | <<1 | Particles: surface wetness, stickiness, microscale roughness, electrostatic attraction<br>Gases: numerous chemical and biological factors as they interact with pollutants having various properties[a] | All with medium or high research potential identified in Table 1 |
| $r_f$, resistance of quasi-laminar layer enveloping surface elements | ~0.005 | Particle deposition as affected by impaction and diffusion[a] | Wind-tunnel studies plus all small-area field flux-parameterization techniques (C.1.b. in Table 1) |
| $r_g$, bulk surface resistance, composed mainly of $r_e$'s and $r_f$'s | <30 | Relationship of mean vertical aloft to transport to individual surface elements | Micrometeorological techniques[b] applied in conjunction with leaf washing, tracer studies, mass-balance studies, and similar methods |
| $r_a$, aerodynamic resistance in the atmospheric surface layer | ~50, day<br>~ 5, night | Similarity theory applied to vertical gas transport[c]; Transport in very stable conditions[c] | All micrometeorological techniques[b] |
| $r_a$, and $r_f$ as affected by medium-scale surface discontinuities | <30 | Increased aerodynamic roughness, Increased aeration of plant | Complex geometry[d]: box-budget studies, airborne eddy-correlation, atmospheric radioactivity, mass balance studies<br>Simple geometry[d]: wind-tunnel studies, tracer studies |
| $r_b$, resistance in the planetary boundary layer | ~1500, day<br>~ 100, night | Vertical flux divergences due to physical and chemical processes | Box-budget studies, airborne eddy correlation |

[a]probably where initial research emphasis should be placed
[b]the gradient, modified Bowen-Ratio, eddy-correlation, variance, and eddy-accumulation methods
[c]not felt to be particularly important in research presently needed
[d]not specifically considered at the workshop

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Next to the actual surface is the quasi-laminar boundary layer with a resistance $r_\ell$ often considered separately. A considerable amount of wind-tunnel work has been performed on phenomena of this scale size. If possible, both laboratory and theoretical studies should consider the high levels of atmospheric turbulence and its effects on the interfacial air layer. For example, the intermittent penetration of strong gusts into deep plant canopies during unstable conditions strongly modifies both the concentration of certain pollutants and the thickness of the boundary layers of air around surface elements.

A difficult theoretical and experimental problem concerns the process by which transfer to surface elements is added up to yield the total deposition from the atmosphere. Micrometeorological techniques usually only yield an estimate of bulk surface resistance ($r_s$ in Table 2) that may not be adequate by itself to identify the controlling process. For present purposes, the goal sought should be simple parameterizations of bulk surface and interfacial sublayer resistances or filtration efficiency. Both numerical and analytical models have been attempted; they usually rely to some extent on empirical relationships found in laboratory and field work. A by-product of such models is the calculation of the accumulation of harmful pollutants to parts of the surface.

On the largest scale sizes, those concerning $r_a$ and $r_b$ in Table 2, application of the parameterizations gives deposition velocites for uniform surfaces; the deposition rates for large diverse areas are computed as an average of contributions from each surface weighted in proportion to the total area covered by each surface. Several sources of error can affect the estimates. For example, the fluxes themselves alter the concentrations, so that use of a single concentration for many types of surfaces is inaccurate. Also, the effects of surface discontinuities may result in altered deposition rates near boundaries of an area with a single type of surface. Obstacles such as trees and isolated buildings have an effect, not to mention the unknown extent to which complex terrain can alter the parameterizations. Obviously, experimental and theoretical methods used to assess these effects should be developed further. Perhaps box-budget experiments can be used to determine errors; such procedures may in the future be sensitive enough to detect the large errors that are of greatest concern.

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## APPENDIX C

## DISSENTING VIEWS

**DISSENTING VIEW #1: Mr. Franz Burmann and Dr. Richard J. Thompson**

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

September 15, 1980

Comments on the Report of the "U.S. EPA Workshop on Dry Deposition Methodology"

Dr. Franz Burmann
Dr. Richard J. Thompson
Dr. Jack L. Durham

Dry deposition measurement methodology is a combination of two disciplines: (1) the micrometeorological measurement or inference of air transport parameters, and (2) quantitative chemical analysis. The workshop has critiqued various methods mainly from the viewpoint of physical mass transport parameters, which is expected since most of the workshop participants were micrometeorologists. The degree of accuracy of chemical analysis is stated for several of the techniques; however, the unreasonable difficulty of such demands on the chemical analyst is not discussed.

While a legitimate need may exist to monitor the "dry deposition of pollutants, especially the strong mineral acids" (see the Preface), known atmospheric chemical behavior is ignored in regard to the preservation of sample integrity. For example, the presence of strong mineral acids in fine aerosols has been demonstrated; however, the presence of such acids in a dry deposition sample (from a bucket, plate, or filter collector) is highly improbable because eventual neutralization by ambient ammonia will occur over the collection period (several days). Of at least equal importance is the simultaneous collection of large mineral particles that are bases, which neutralize the acids during extraction. Our previous experience has been that dust-fall bucket samples invariably yield a basic aqueous extract. Such a result is contrary to the suspected acidification of surface waters in the northeast.

Not demonstrated is the requirement of non-surrogate surface dry deposition measurement procedures to be able (a) to detect mean concentration differences of 1 to 10% in successive samples to within an accuracy of 10%, or (b) to monitor pollutant air concentrations with a response time of one second or less. However, if such requirements are valid, the successful achievement of chemical/physical measurements in a routine monitoring network is an unreasonable expectation. In general the error in flowrate measurement for aspirated samples is not better than ±10%. If this fluctuation error could be reduced to ±1% (which is unlikely), the chemical measurement random errors are expected to be too large to be acceptable. For example, the uncertainties of the NBS analysis of urban particulate Standard Reference Material 1648 are (see attachment):

| | |
|---|---|
| Nitrogen ($NO_3^-$) | $2\sigma$ = 1.07% ± 0.06 |
| Nitrogen ($NH_4^+$) | $2\sigma$ = 2.01% ± 0.08 |
| Sulfate | $2\sigma$ = 15.42% ± 14 |

Thus, the precision of the chemical analyses for nitrate and ammonium may be sufficient (disregarding biases due to sample volatility), but that for sulfate is unacceptable. It is not reasonable to expect that the analysis of routine network samples can be performed at significantly lower levels of random error than obtained by NBS for urban aerosols.

Also, the determination of sample acidity should be expected to have errors much larger than those for sulfate, principally because the environmental sample will contain a complex mixture of strong and weak acids and bases.

It is notable that the report does not endorse a reliance or expanded use of surrogate surfaces, including the dry dust bucket. Also, no functional definition of dry deposition is made which would permit effective monitoring, except for sophisticated research methods dependent upon the chemical analyses of samples at a relative standard error of ± 1%, or the analysis of ambient concentration fluctuations at 1 Hz. In general, the chemical analysis methods cannot provide the required precision, and the chemical monitors do not possess sufficiently rapid response.

CONCLUSION: The report does not identify for routine monitoring suitable methodology that is presently in existance. Recommendations are given for the development of dry deposition monitors based on fundamental principles of micrometeorology and analytical chemistry. The extreme requirements for precision/response time of the chemical analysis/monitor make it unlikely that such methods will be developed rapidly, as evidenced by the total absence of even one routine dry deposition monitor based on eddy accumulation, modified Bowen ratio, or variance techniques.

Attachment

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

# National Bureau of Standards Certificate of Analysis

## Standard Reference Material 1648

### Urban Particulate Matter

This Standard Reference Material is intended for use in the calibration of methods used in the chemical analysis of atmospheric particulate matter and materials with similar matrices. The material is atmospheric particulate matter collected in an urban location.

The certified values are based on measurements of 6 to 30 samples by each of the analytical techniques indicated. The estimated uncertainties include those due to sample variation, possible methodology differences, and errors of measurement (see Preparation and Analysis). The certified values are based on a sample size of at least 100 mg of the dried material. The material should be dried at 105 °C for 8 hours before use.

| Element | µg/g | Element | Weight % |
|---|---|---|---|
| Arsenic[c c] | 115 ± 10 | Iron[a b c e] | 3.91 ± 0.10 |
| Cadmium[a b c d] | 75 ± 7 | Lead[a b d] | 0.655 ± .008 |
| Chromium[b c] | 403 ± 12 | | |
| Copper[a b e] | 609 ± 27 | | |
| Nickel[a b d] | 82 ± 3 | | |
| Zinc[a b c d] | 4760 ± 140 | | |
| Uranium[b] | 5.5 ± 0.1 | | |

a. Atomic Absorption Spectrophotometry
b. Isotope Dilution Mass Spectrometry
c. Neutron Activation Analysis
d. Polarography
e. Spectrophotometry

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
November 16, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

## Preparation and Analysis

This SRM was prepared from urban particulate matter collected in the St. Louis, Missouri, area in a baghouse especially designed for this purpose. The material was collected over a period in excess of 12 months and, therefore, is a time-integrated sample. While not represented to be typical of the area in which it was collected, it is believed to typify the analytical problems of atmospheric samples obtained from industrialized urban areas.

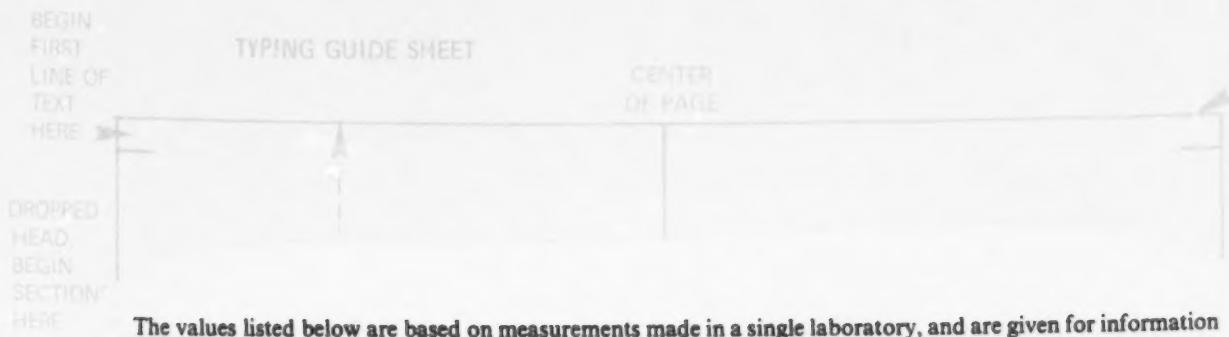
The material was removed from the filter bags by a specially designed vacuum cleaner and combined into a single lot. This product was screened through a fine-mesh sieve to remove most of the fibers and other extraneous material from the bags. The sieved material was then thoroughly mixed in a V-blender, bottled, and sequentially numbered.

Randomly selected bottles were used for the analytical measurements. Each analyst examined at least 6 bottles, some of them measuring replicate samples from each bottle. No correlation was found between measured values and the bottling sequence. Also, the results of measurements of samples from different bottles were not significantly different than the measurements of replicate samples from single bottles. Accordingly, it is believed that all bottles of this SRM have the same composition.

The analytical methods employed were those in regular use at NBS for certification of Standard Reference Materials, except as noted in the following paragraphs. Measurements and calibrations were made to reduce random and systematic errors to no more than one percent, relative. The uncertainties of the certified values listed in the table include those associated both with measurement and material variability. They represent the 95 percent tolerance limits for an individual sub-sample, i.e., 95 percent of the sub-samples from a single unit of this SRM would be expected to have a composition within the indicated range of values 95 percent of the time.

The following values have not been certified because either they were not based on results of a reference method, or were not determined by two or more independent methods. They are included for information only. All values are in units of $\mu g/g$ of sample, unless otherwise indicated.

| | | | |
|---|---|---|---|
| Aluminum | (3.3 wt. %) | Lanthanum | (42) |
| Antimony | (45) | Magnesium | (0.8 wt. %) |
| Barium | (737) | Manganese | (860) |
| Bromine | (500) | Potassium | (1.0 wt. %) |
| Cerium | (55) | Samarium | (4.4) |
| Cesium | (3) | Scandium | (7) |
| Chlorine | (0.45 wt. %) | Selenium | (24) |
| Cobalt | (18) | Silver | (6) |
| Europium | (0.8) | Sodium | (0.40 wt. %) |
| Hafnium | (4.4) | Thorium | (7.4) |
| Indium | (1.0) | Titanium | (0.40 wt. %) |
| Iodine | (20) | Tungsten | (4.8) |
| Vanadium | (130) | | |




The values listed below are based on measurements made in a single laboratory, and are given for information only. While no reason exists to suspect systematic bias in these numbers, no attempt was made to evaluate such bias attributable to either the method or the laboratory. The method used for each set of measurements is also listed. The uncertainties indicated are two times the standard deviation of the mean.

| | |
|---|---|
| Nitrogen ($NO_3$) | (1.07% ± 0.06) |
| Nitrogen ($NH_4$) | (2.01% ± .08) |
| Sulfate | (15.42% ± .14) |
| $SiO_2$ | (26.8% ± .38) |
| Freon Soluble | (1.19% ± .47) |

The above values were determined by the methods indicated below:

Nitrate – Extraction with water and measurement by ASTM Method D992.

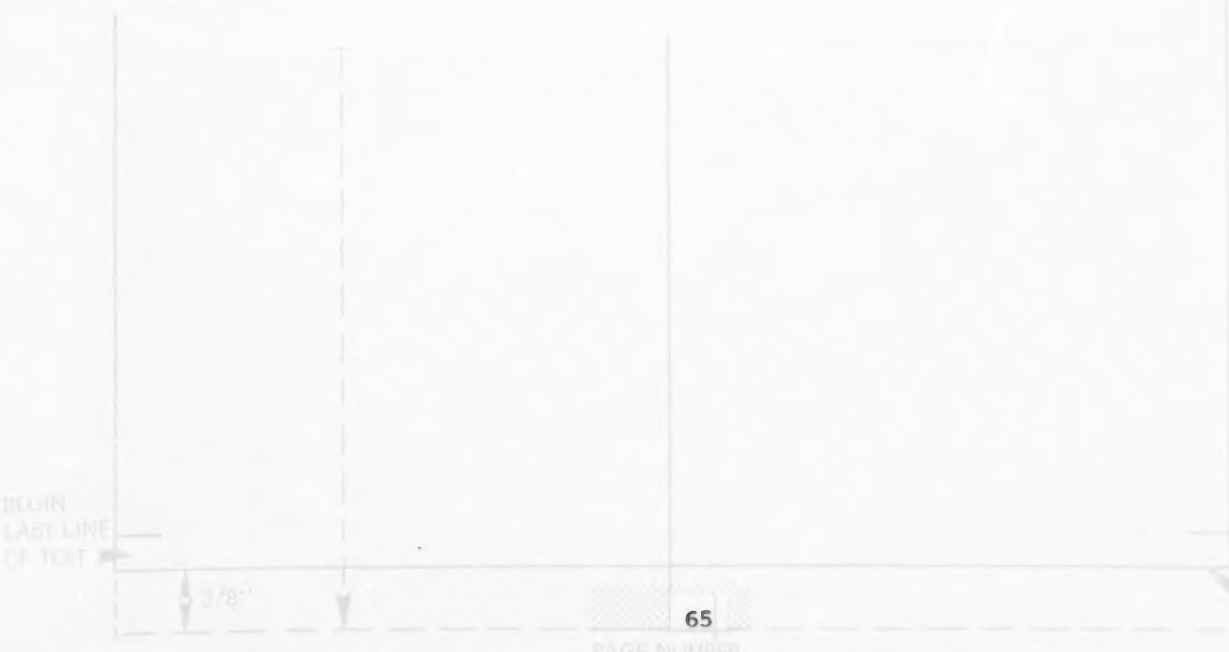
Ammonia – NaOH addition followed by steam distillation and titration.

Sulfate – Extraction with water and measurement by ASTM D516.

$SiO_2$ – Solution and measurement by ASTM Method E350.

Freon Soluble – Extraction with Freon 113, using the method described in "Standard Methods in Examination of Water and Waste Water," 14th Edition, p. 518, American Public Health Association, Washington, D.C.

J. W. Matwey supervised the collection of the material as well as sieving and bottling. The following members of the staff of the NBS Center for Analytical Chemistry performed the certification measurements: R. W. Burke; E. R. Deardorff; B. I. Diamondstone; L. P. Dunstan; M. S. Epstein; M. Gallorini; E. L. Garner; J. W. Gramlich; R. R. Greenberg; L. A. Machlan; E. J. Maienthal; and T. J. Murphy.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**DISSENTING VIEW #2: Dr. Cliff I. Davidson and Steven E. Lindberg**

## ALTERNATIVE VIEWPOINTS ON SURROGATE SURFACES

Surrogate surface deposition measurements of various types have been conducted for years, and will probably continue to be used on a widespread basis. Simplicity in obtaining the data, control over contamination, ability to collect sufficient material for trace level analysis, and low expenses are the primary reasons. It is acknowledged that certain applications of such measurements in particular may not provide as much accuracy as more sophisticated techniques, *however sufficient data are not available to establish conclusively that all types of surrogate surfaces should not be used.*

Several surrogate surface studies reported in the literature have shown consistencies in the data which suggest that semi-quantitative information can be obtained. For example, Peirson et. al. (1973) showed dry deposition velocities in the range of 0.2-0.6cm/sec for 15 out of 23 trace elements studied. Horizontal sheets of filter paper were used for these measurements. Clough (1973) has determined the relationship between deposition velocities measured using similar filter samplers in a wind tunnel with theoretical deposition velocities for smooth surfaces and a grass sward as influenced by particle size and wind speed. Similar experiments were reported by Klepper and Craig (1975) using 0.8 μm radioactively labelled aerosols to compare deposition velocities to bean leaves and inert surfaces (tape). Deposition velocities for leaves were similar to those measured for upward facing inert surfaces under the conditions tested. A comparison of deposition to vegetation with

that to surrogate surfaces has also been reported by Servant (1976) who used inverted plastic containers and leaves from four species of trees.

Huntzicker et. al. (1975) used teflon plates to measure lead dry deposition in the Los Angeles Basin. It was found that the dry deposition rate was similar within the Basin, and decreased at several sites monotonically with distance away from the Basin when plates were set up in surrounding mountain, desert, and coastal areas. Lead deposition also decreased monotonically between 1m and 150m from a freeway near central Los Angeles.

In another Los Angeles area study, Davidson (1977) measured simultaneously airborne size distributions and teflon plate deposition of lead, zinc and cadmium. It was shown that the size data could be used with equations for sedimentation to predict deposition on the plates. This suggests that teflon plate data can provide a reliable lower limit to dry deposition on natural surfaces under certain conditions, such as when sedimentation is the dominant transport mechanism onto the plates.

Lindberg et. al. (1979) compared in-canopy petri dish dry deposition data for several atmospheric constituents to that obtained by leaf washing experiments in a deciduous forest (Walker Branch Watershed, Tennessee). Agreement to within a factor of two was obtained for cadmium, zinc, manganese, and sulfate, although poorer agreement was observed for lead (factor of 10). Leaf surface absorption, rather than nonrepresentative petri dish data, could be a possible reason for the discrepancies in the Pb values. This study also showed consistently higher dry deposition velocities, based on petri dish data, for those elements found in larger particle sizes. The deposition velocity for particulate sulfate to flat plates when extrapolated to the full

forest canopy at Walker Branch is in rough agreement with values for the total sulfur dry deposition velocity to a pine forest canopy determined by eddy correlation techniques (Hicks and Wesely, 1978).

Comparisons between airborne particle size data and teflon plate deposition have been conducted by Elias and Davidson (1980) in a remote High Sierra canyon. As in the Tennessee study, consistently greater dry deposition velocities were found for those elements associated with larger particle sizes. Values of dry deposition velocity for each element were also consistent from one experiment to the next.

The data from these studies do not provide detailed information on the relations between surrogate surface and natural surface deposition. The consistencies in the data, however, suggest that it may be possible to establish such relations, i.e., to calibrate surrogate surfaces in some fashion. We do not suggest that these surfaces be used to predict airborne concentrations, however. Uncertainties associated with these relationships cannot be predicted at this time.

We suggest that the comparison of surrogate surface, micrometeorological, leaf washing, and other methods to estimate dry deposition be performed in wind tunnels and in the field over natural surfaces. This would be especially useful for those dry collectors that have already been applied in a research mode (e.g., teflon discs, polyethylene plates, or filter paper).

Recommended research includes determination of the relationships among material suspended in the atmosphere, collected by surrogate surfaces, and deposited on natural surface elements (as determined by washing and microscopic examination, or other techniques). Such comparison studies might lead to a better design and application of

certain artificial surfaces than those routinely used for monitoring, such as the use of flat plates situated in the foliar canopy as opposed to the use of buckets at ground level.

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